İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF TRIPHENYL PHOSPHINE OXIDE CONTAINING POLYMERS VIA ATRP

M.Sc. Thesis by
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Department : Polymer Science and Technology

Programme: Polymer Science and Technology

AUGUST 2005

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Date of submission : 10 August 2005

Date of defence examination: 11 August 2005

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AUGUST 2005

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TRİFENİL FOSFİN OKSİT İÇEREN POLİMERLERİN ATRP İLE SENTEZİ

YÜKSEK LİSANS TEZİ

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Tezin Enstitüye Verildiği Tarih : 10 Ağustos 2005

Tezin Savunulduğu Tarih : 11 Ağustos 2005

Tez Danışmanı : Prof.Dr. İ. Ersin SERHATLI (İ.T.Ü.)

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Prof.Dr. Atilla GÜNGÖR (M.Ü.)

AĞUSTOS 2005

ACKNOWLEDGEMENT

This master study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), located at Faculty of Science and Letters in İstanbul Technical University.

I would like to thank my advisor, Professor Dr. İ. Ersin SERHATLI, for his guidance, inspiration and encouragement throughout this work, and for the opportunity to work in his research group.

Special thanks go to Prof. Dr. Ayşen ÖNEN for her good suggestions, invaluable help, and support .

I would like to acknowlegde Prof. Dr. Atilla GÜNGÖR sharing his knowledges and experiences with me generously throughout this research.

I would like to acknowledge Dr. Sevim KARATAŞ for her great generous help during preparation of this thesis.

Many thanks go to my colleagues in this great research group for their assistance and friendship. I would like to especially acknowledge Mehmet Cenap ÇETİNTAŞ, Tuba ÇAKIR, Mevzun YÜKSEL, and Alev KÖPRÜLÜLÜ.

Finally, I would like to offer the most gratitude to my parents for their patience, understanding, moral support and encouragement during all stages in the preparation of this thesis.

August 2005 Betül TÜREL

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LIST OF ABBREVIATIONS

CRP	**:**	Controlled / "Living" Free Radical Polymerization
NMP	**:**	Nitroxide Mediated Polymerization
ATRP	**:**	Atom Transfer Radical Polymerization
ATRA	**:**	Atom Transfer Radical Addition
RAFT	**:**	Reversible Addition-Fragmentation Chain Transfer
TEMPO	**:**	2,2,6,6-tetramethyl -1-piperidinyl-1-oxy
PMDETA	**:**	N**,**N,N,N',N''pentamethyldiethylenetriamine
St	**:**	Styrene
MMA	**:**	Methylmethacrylate
BFPPO	**:**	Bis(4-fluorophenyl)phenyl phosphine oxide
BOHPPO	**:**	Bis(4-hydroxyphenyl)phenyl phosphine oxide
BOHEPPO	**:**	Bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide
BBEPPO	**:**	Bis [(4-β-(2-bromopropanoate)ethoxy)phenyl] phenyl phosphine oxide
DMSO	**:**	Dimethyl sulfoxide
PSt	**:**	Polysytrene
PMMA	**:**	Polymethyl methacrylate
UV	**:**	Ultra-Violet
DSC	**:**	Differential Scaning Calorimetry
^{1}H-NMR	**:**	Nuclear Magnetic Resonance
GPC	**:**	Gel Permeation Chromatography
TGA	**:**	Thermogravimetrical Analysis

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LIST OF SYMBOLS

$\mathbf{M_n}$	**:** Number Average Molecular Weight
$\mathbf{M_w}$	**:** Weight Average Molecular Weight
$\mathbf{M_w / M_n}$	**:** Molecular Weight Distribution
$\mathbf{DP_n}$	**:** Degree of Polymerization
$\boldsymbol{\lambda}$	**:** Wavelength
$\mathbf{k_a, k_d}$	**:** Rate constants of activation and deactivation steps of the initiation in radical polymerization
$\mathbf{K_{eq}}$	**:** Equilibrium rate constant and in radical polymerization
$\mathbf{k_p, k_t}$	**:** Rate constant of propagation and rate constant of termination
$\boldsymbol{\lambda}$	**:** Wavelength
Tg	**:** The Glass Transition Temperature

SYNTHESIS OF TRIPHENYL PHOSPHINE OXIDE CONTAINING POLYMERS VIA ATRP

SUMMARY

In the last decade, the ability to synthesize macromolecules with complex and controlled architectures is becoming an increasingly important aspect of polymer science by being able to control the radical polymerization. It is seen a considerable increase in new controlled radical polymerization techniques.
Specifically, controlled architectures possess some characteristics which are molecular weight control, end group control, ability to form block copolymers, and a living nature.

In 1995, Matyjaszewski et al. developed an alternative living radical polymerization process using a copper(I)-catalyzed atom transfer process (ATRP). ATRP systems with copper complexes are widely used basically in polymerization of monomers such as acrylates and styrene.

In this project, Bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide compound will be brominated to form a macroinitiator. This macroinitiator will be used by the presence of Cu(I)/Ligand catalyst system to synthesize styrene and methacrylate polymers.

TRİFENİL FOSFİN OKSİT İÇEREN POLİMERLERİN ATRP İLE SENTEZİ

ÖZET

Son yıllarda radikal polimerizasyon üzerinde kontrol sağlanmasıyla kompleks ve kontrollü mimariye sahip makromoleküllerin sentezi üzerine yapılan çalışmalar, polimer biliminde gittikçe artan bir öneme sahiptir. Yeni kontrollü radikal polimerizasyon tekniklerinin gelişmesinde gözle görülür bir artış gözlemlenmektedir. Kontrollü mimari denilince, molekül ağırlığı kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme yeteneği ve yaşayan karakter akla gelmektedir.

1995 yılında Matyjaszewski ve grubu Atom Transfer Radikal Polimerizasyonunu (ATRP) gerçekleştirmişlerdir. ATRP, Cu(I) / Ligand sistemi ile katalizlenen yaşayan serbest radikal polimerizasyon sistemidir. Bakır kompleksli ATRP sistemleri başlıca akrilat ve stiren gibi monomerlerin polimerizasyonunda başarıyla kullanılmaktadır.

Bu çalışmada Bis[4-β-hidroksietoksi)fenil] fenil fosfin oksit bileşiğinin bromlama reaksiyonu ile bir makrobaşlatıcı haline getirilecektir. Sentezlenen bu makrobaşlatıcı Cu(I)/Ligand sistemi ile katalizlenerek ATRP ile stiren ve metilmetakrilat polimerleri sentezlenecektir.

1. INTRODUCTION

Free radical polymerizations are generally poorly controlled, producing high molecular weight polymers at the early stages of polymerization and ultimately poorly defined polymers with high polydispersity. In recent years, controlled/living radical polymerization has attracted increased attention because of possibility of overcoming many of these deficiencies. Copper-based atom transfer radical polymerization (ATRP) seems to be the most studied system, one that allows controlled polymerization of styrenes, acrylates, methacrylates, acrylamides, and acrylonitrile[1].

The controlled chain growth and living nature of ATRP make it very useful for the preparation of well-defined block and graft copolymers. ATRP also allows its potential in the synthesis of a new well-defined macromolecular architectures such as comb, star, and dendritic macromolecules [2].

The phosphine oxide group has often been incorporated into polymers to enhance the thermal and thermal/oxidative stability and inginiton resistance of polymer matrices[3]. Also phosphorus containing compounds are known fire retardants.[4-7].

This thesis will describe new research studies which have been directed towards the synthesis of polymers via ATRP with a new macroinitiator and the investigation of their molecular weigts, and thermal behavior.

A new initiator bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide have been sythesized and used in ATRP to prepare polymers.

2. THEORETICAL PART

2.1 Overview of Phosphorus Chemistry

2.1.1 Introduction

Excellent books are available on the fundamental features of organophosphorus chemistry [8,9]. Moreover, the incorporation of phophorus into polymers has been discussed [10]. Figure 2.1 illustrates various classes of organophophorus compounds. The focus of this section will be to give an overview of different synthetic routes for the synthesis of hydrolytically stable carbons bonded to phosphorus, such as phosphines and phosphine oxides.

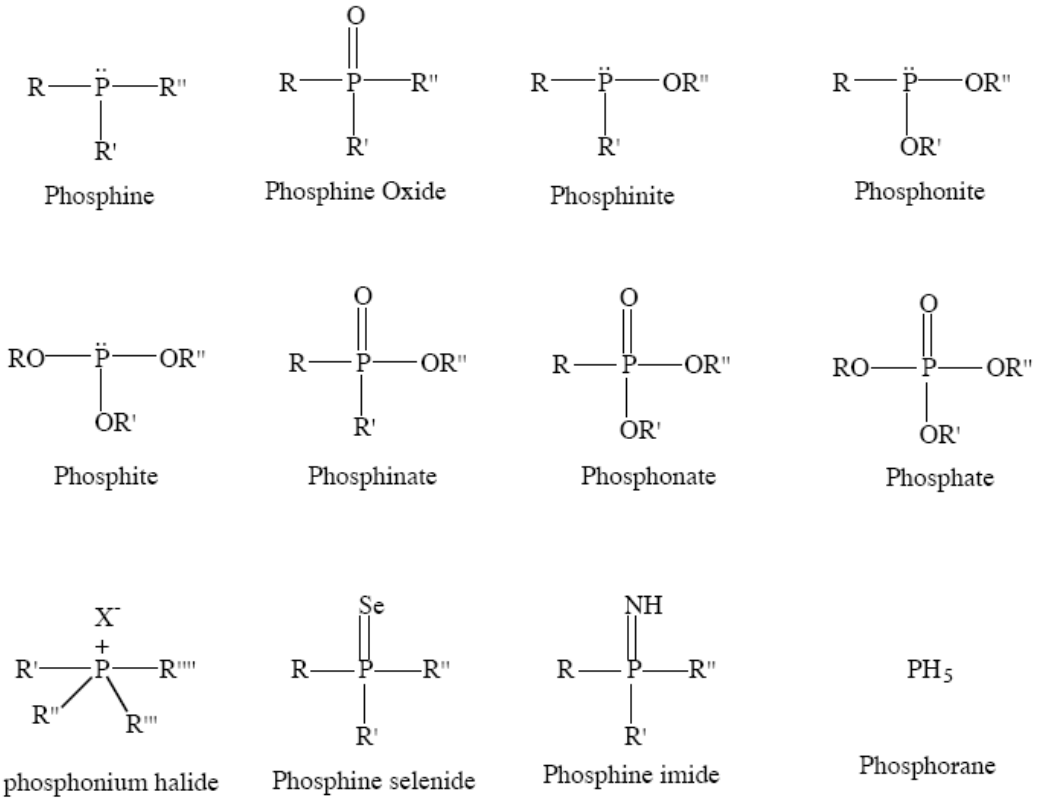


Figure.2.1 Nomenclature for selected classes of phosphorus compounds

Phosphorus compounds have found many important commercial applications including fertilizer in the form of $CaHPO_4$, along with detergents, animal feed, fire retardants, and even in the pharmaceutical industry. Trivalent phosphorus

compounds have also been utilized as antioxidants and stabilizers in rubbers and plastics.

Phosphorus containing polymers generally possess interesting properties such as high chemical and thermo-oxidative stability and low flammability. In fact, molecules such as triphenylphosphine oxide have been known for quite some time to be thermally stable. A few research groups have prepared polymeric materials containing triphenyl phosphine oxide as flame retardant polymers[11].

Since polymers containing phosphorus as an integral part of the backbone efforts have been made to synthesize phosphorus containing polyimides[12]. As a part of an ongoing materials development activity to produce high performance polymers that are durable to the space environment, phosphine oxide containing polyimides have been under investigation[13].

Utilizing the aryl phosphine oxide moity as X is feasible because of its electron withdrawing characteristics and because it contributes to several high performance properties. Poly(arylene ether phosphine oxide)s display high thermal stability and inherent flame resistance and have also shown potential as high temperature matrix resins and/or adhesives [14].

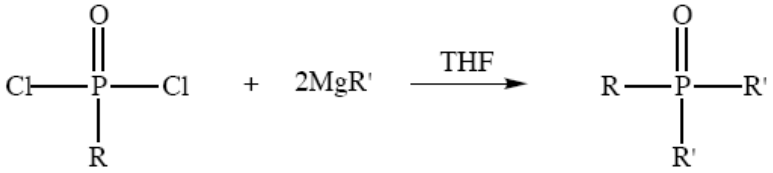
2.1.2 Synthetic Routes for the Synthesis of Phosphines and Phosphine Oxides

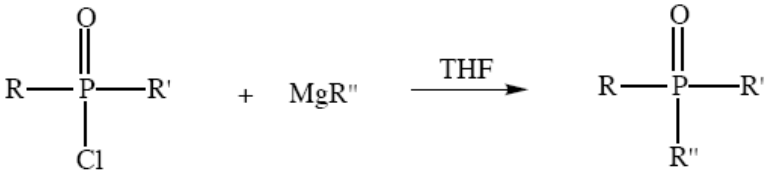
Phosphines may be synthesized using a variety of techniques including Grignard and organolithium reagents. The synthesis of phosphine using Grignard chemistry starting with phosphorus trichloride follows the form of the equation below [8].

$$PCl_3 + 3\,RMgX \longrightarrow R_3P + 3\,MgXCl$$

The phosphorus halide is added to the preformed Grignard reagent in this reaction. After hydrolysis the product is usually seperated using ether and purified [10]. Grignard synthesis allows for high yields with non-sterically hindered phosphines and primary or aryl Grignard reagents [8,10]. Organolithium compounds are the reagents of choice if steric hindrance is important. Attempted synthesis using secondary or tertiary halides produce only low yields of tertiary phosphine [10]. This Grignard chemistry can also be applied to the synthesis of phosphine oxides; for

example, Kormachev *et al.*[10] showed that dialkylaryl and alkylaryl phosphine oxides could be synthesized using alkyl Grignard reagents, as illustrated by the equations below.





A wide variety of phosphines and phosphine oxides have been synthesized utilizing Grignard chemistry and only a selected few are shown in Figure 2.2.

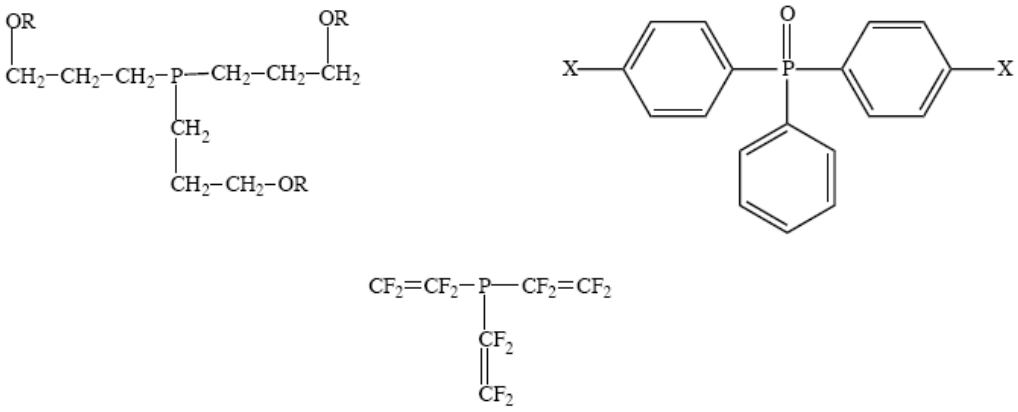


Figure 2.2 Examples of phosphorus containing compounds sythesized *via* Grignard Chemistry

Phophines may also be synthesized using organolithium reagents [10]. The synthesis of phosphines using organolithium reagents follows the form of the equation below.

$$3RLi + PCl_3 \longrightarrow R_3P + LiCl$$

Organolithium compounds undergo similar reactions as Grignard reagents; however they are much more reactive since the carbanion derived from a C-Li bond is more basic than of the C-Mg bond [15]. The organolithium route is preferred for synthesis

of sterically hindered phosphines such as tri-tert-butylphosphine [10]. A wide variety of sterically hindered phosphines have been synthesized using organolithium chemistry and several examples are shown in Figure 2.3

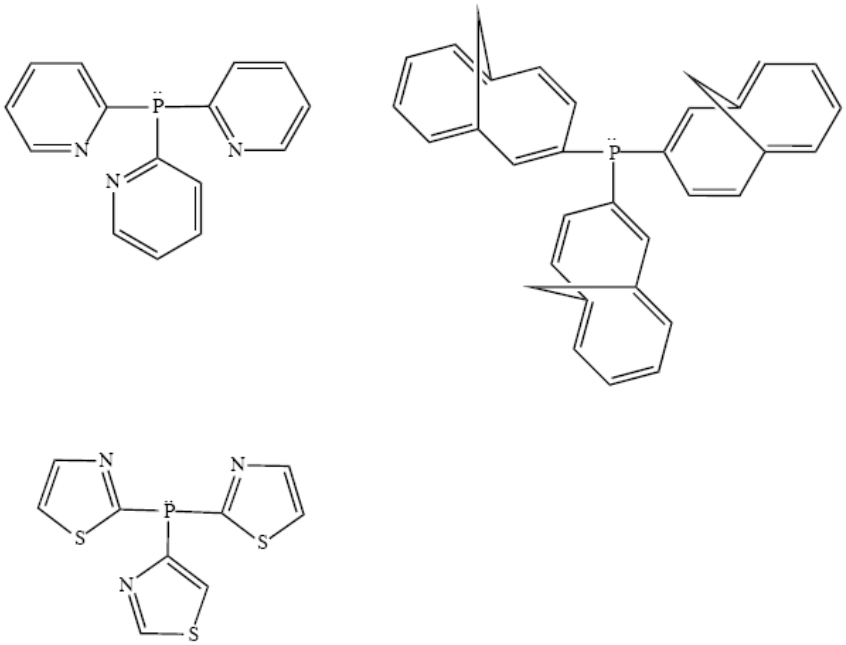


Figure 2.3 Selected sterically hindered phosphines synthesized using organolithium reagents [8]

In addition, various phosphines and phosphine sulfides may be synthesized *via* electrophilic substitution using Friedel-Crafts chemistry. In this electrophilic synthesis, the starting material is generally a mono-di-or tri-halophosphine or phosphine sulfide. In the case of thiophosphorus trichloride ($PSCl_3$) it is possible to perform sequential additions of benzene or substituted benzene reagents to prepare compounds of the structure bis(R)R'phosphine sulfide [10]. Therefore, it is possible to prepare such a compound from thiophosphorus trichloride by first reacting $P(S)Cl_3$ with a slight excess of R and then subsequently with excess R'. This reaction has been studied in detail by Weiss and Kliener as shown in Figure 2.4. Similar work has also been carried out by Wescott for involving the synthesis of 4,4'bis(fluorophenyl) phenylphosphine sulfide using analogous chemistry [10].

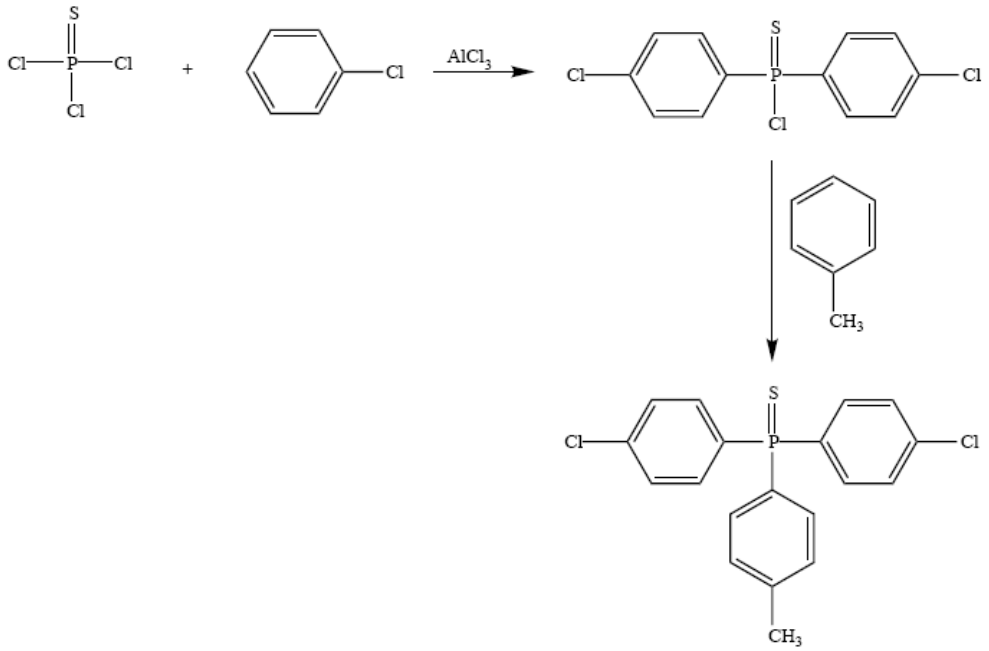


Figure 2.4 Illustration of the synthesis of a trisubstituted phosphine sulfide *via* subsequent addition of reagents

2.2 Flame Resistance in Polymeric Materials

2.2.1 Modification of Polymers to Improve Flame Resistance

Organic polymers are one of the most versatile and widely utilized class of materials used today, and are used in many applications ranging from adhesives, aircraft interiors, and electronic components [10]. However, except for a limited number of socalled inherently flame resistant polymers, such as polytetrafluoroethylene (Teflon), polyvinyl chloride, etc., thermoplastics are not generally flame resistant. However, the flame resistance of polymers has been improved using two different techniques: (1) by physically blending flame retardant additives such as Sb_2O_3 in combination with brominated aromatics or various phosphates with the polymer, and (2) by incorporating flame retardant structures into a polymeric backbone [10]. The introduction of phophorus compounds as flame retardant in polymers is well known [16]. Most flame retardants are introduced as physically blended additives and are not chemically bonded to the polymer. Such additives can potentially be leached out of the material, which may introduce loss of protection and/or undesired hazards. Phosphorus containing comonomer flame retardants incorporated into the polymer backbone may overcome this problem [16]. Flame retardant additives used in

synthetic polymers include organic halogen and organic phosphorus compounds [17]. A flame retardant additive interferes with one or more of the steps of the combustion cycle, including heating of the polymeric material, its subsequent degradation, and the further combustion of volatiles that may be generated [10].

While a flame retardant additive may function at one or more of these three steps, it is preferred that the additive function at more than one step. For example, it may inhibit combustion at Step 1 by forming a glass-like coating, which should preferably have low thermal conductivity on the surface of the material upon exposure to heat. The additive may also degrade endothermically, thereby absorbing energy from the polymer [10]. During the ignition stage, these flame retardant additives may also deactivate highly reactive radical propagating species that result from chain scission during the combustion process [18], as is illustrated below in Figure 2.5 [19]. The flame retardant additives may function in a similar manner as in the second stage by reacting with radicals during the combustion of volatile to quench the propagating nature of the fire.

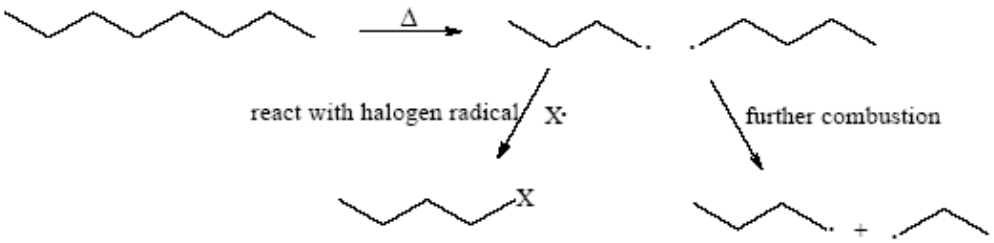


Figure 2.5 Ilustration of how halogens can interrupt the combustion cycle.

The effectiveness of the halogen depends on many factors, including the halogen used, the polymeric structure and the concentration of halogen. The effectiveness of the halogen follows the order Br>Cl>F, and generally large amounts of halogen (between 15-30 wt. %) are required [10]. Moreover, those halogens bonded to aliphatic carbons are better flame retardants than aromatic halogens [20]. This is probably due to that fact that aliphatic halogens degrade at a lower temperature via a radical mechanism than aromatic halogens. However, there are problems associated with physically blended flame retardant additives. These drawbacks include compatibility issues, problem of the additive leaching out over time, and the fact that the decomposition temperature of the fire retardant needs to be appropriate for a

specific polymeric material. Clough [10] studied the aging effects of ethylene-propylene rubber (EPR) containing various amounts of halogen-hydrocarbon additives combined with Sb_2O_3 and discovered a significant loss of both the halogen additive and the Sb_2O_3 due to aging.

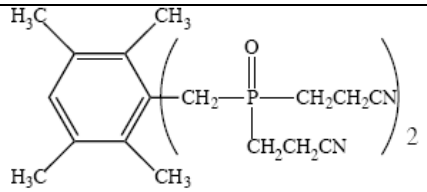
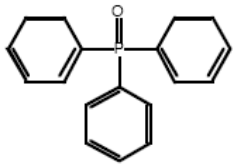
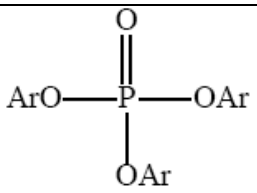
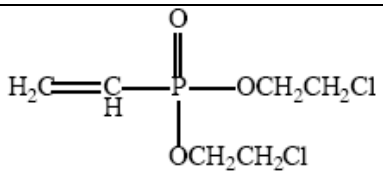
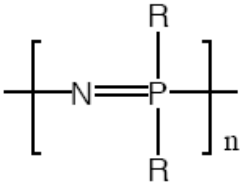
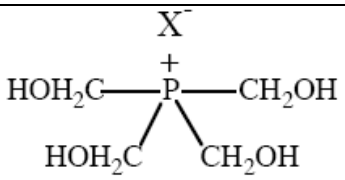
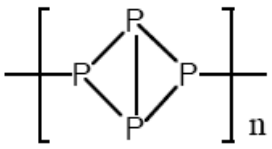
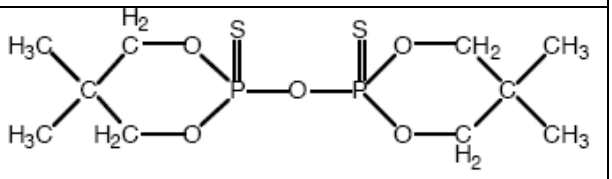
In order to avoid the problem of aging, one may add halogens bonded to the backbone of the thermoplastic. This is particularly true for polyolefins [21] and epoxies [22,23]. This incorporation has resulted in an increased char yield and a higher limiting oxygen index, which is one of the often used measurement methodologies [22]. Commercially, tetrabromobisphenol-A or its diglycidylether are often used to cure epoxies for use in printed circuit boards and other applications where fire resistance is needed [23].

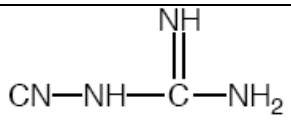
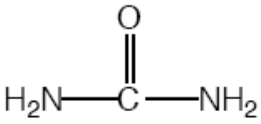
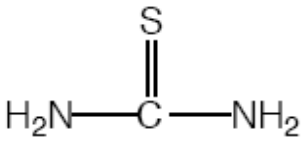
The disadvantage of halogen based flame retardants is the fact that toxic gases of the form HX are emitted upon combustion. Phosphorus or nitrogen containing additives, as well as others, are being investigated as a possible way to overcome this problem [10]. A survey of phosphorus and nitrogen containing flame retardant additives is listed in Table 2.1.

The incorporation of functionalized derivatives of triphenylphosphine oxide into a variety of polymers has recently been investigated [16]. For example, the polycarbonate derived from bisphenol A and phosgene is an important engineering thermoplastic and incorporation of various phosphorus compounds into the backbone have been examined[16].

Chemical incorporation of reactive phosphorus comonomers into the polymer backbone has been reported that phosphorus containing aliphatc diamines and dicarboxylica acids have been successfully incorporated into polamides to improve flame resistance [24].

Table 2.1 Examples of Phosphorus and Nitrogen Containin Flame Retardant Additives

Class of Additive	Structure
Phosphine oxide	
Triphenyl phosphine oxide	
Triaryl phosphanates	
Vinylphosphanates	
Polyphosphazenes	
Phosphonium Salts	
Red Phosphorus	
Phosphine Sulfide	
Cyanamide	

Dicyanamide	
Urea	
Thiourea	
Ammonium Salt	NH_4SCN

Phosphorus containing flame retardants can be either gas phase or condensed phase active. For example, trimethylphosphate, triphenylphosphate, triphenylphosphine oxide, as well as the halogens previously discussed, exhibit vapor phase inhibition. A proposed mechanism for the vapor phase inhibition of phosphine oxide flame retardant additives is provided in Figure 2.6 [25]. This mechanism produces two radical scavengers; a hydrogen radical and an oxygen radical. These radicals can combine with radicals produced during chain scission and inhibit the propagation of the flame front. A similar idea is shown in Figure 2.5.

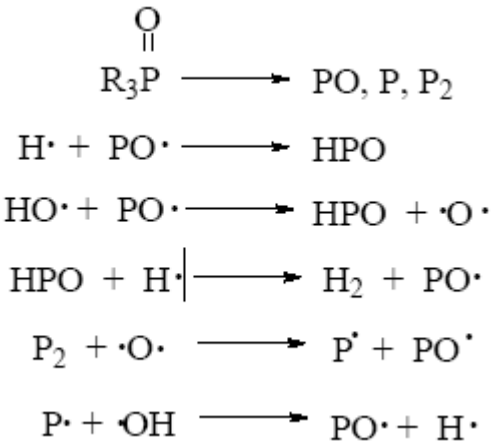


Figure 2.6 Illustration of the vapor phase inhibition mechanism of phosphorus containing flame retardants

Inagaki et al. [10] have shown that there is a linear correlation between the weight percent phosphorus and the limiting oxygen index (LOI) for cotton samples treated

with phosphorus containing flame retardants. The LOI is an empirical technique developed to estimate the amount of oxygen in an oxygen/nitrogen atmosphere that is required to sustain a flame. Thus, the higher the LOI value, the more flame resistant the material is. [21]. In general, these studies show that as the amount of phosphorus is increased, the LOI increased linearly within the range tested.

Phosphorus containing fire retardants may also behave as condensed phase inhibitors [22, 25]. Condensed phase inhibition involves changes in the polymer substrate to promote crosslinking and the formation of a char, serving two purposes. Firstly, it behaves as an insulating layer protecting the underlying polymer from the heat and flame. Secondly, it can act as a barrier preventing oxygen from reaching the uncombusted polymer, therefore inhibiting further combustion. Figure 2.7 below illustrates how phosphorus can behave as a condensed phase flame retardant [25].

Organophosphorus compounds containing P-O-C bonds can thermally or hydrolytically degrade to phosphorus acids. These acids then react with cellulose to form a phosphorus ester. The phosphorus acid can also catalyze dehydration of an organic species, leading to increased unsaturation and increased char formation. When a phosphorus aryl compound is incorporated into the backbone of a polymer, the phosphorus forms a char consisting of a phosphorus anhydride type structure, which inhibits combustion via a condensed phase mechanism [10]. The condensed mechanism is preferred because it offers the advantages of a material with lower flammability without the release of toxic gases, such as HX, and does not require as large a loading as is needed for the vapor phase mechanism. Table 2.2 shows a variety of polymers that have phosphorus incorporated within their backbones.

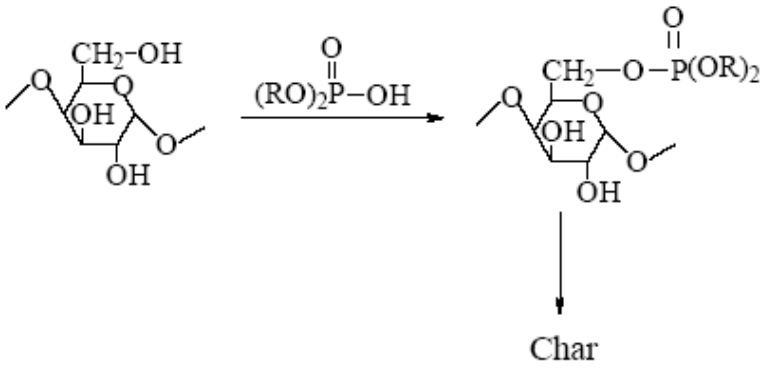
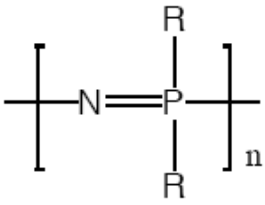
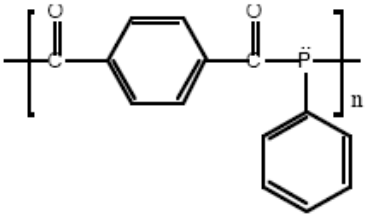
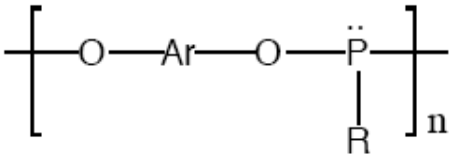
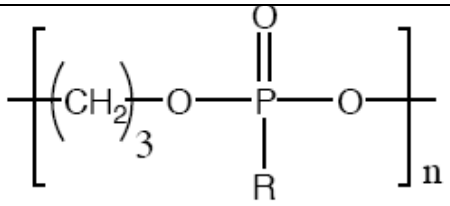
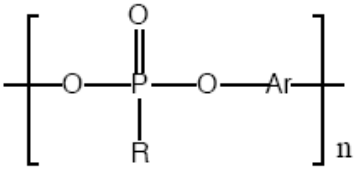
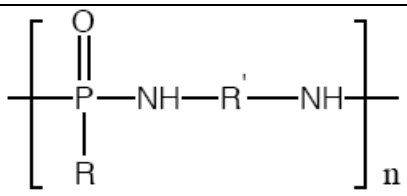
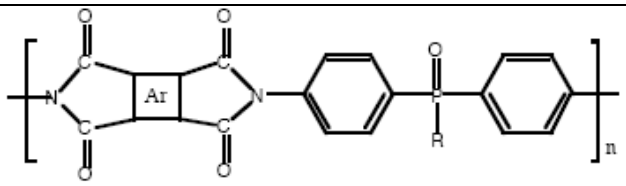
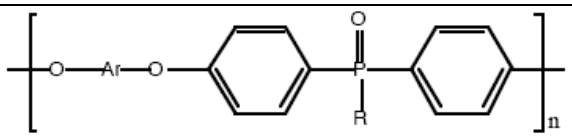
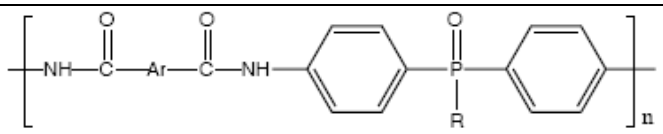
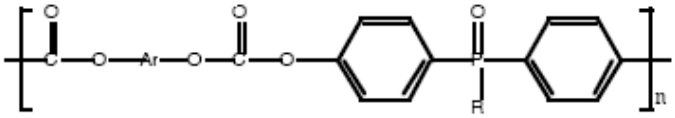
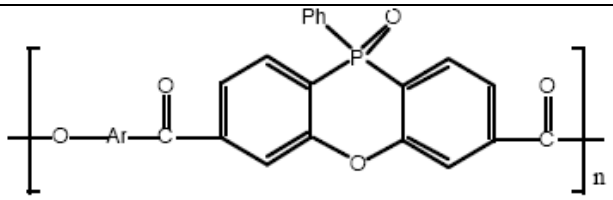


Figure 2.7 Illustration of how a phosphorus flame retardant may induce char

Table 2.2 Illustration of the Variety of Polymers Containing Phosphorus

Polymer Class	Polymer Structure
Phosphazines	
Polyphosphine	
Polyphosphonite	
Polyphosphonate	
Polyphosphonate	
Phosphorus amide	
Polyimide	
Poly(arylene ether)	

Polyamide	
Polycarbonate	
Polyester	

Another area of interest is the actual mechanism of char formation and how to induce high char yields in polymers to enhance flame resistance [10]. Figure 2.8 illustrates a proposed mechanism for char formation [26], wherein a polymer is thermally decomposed *via* chain scission. After this initial decomposition step, the polymer may either undergo further decomposition or react with another polymer chain to form a crosslinked network. If the polymer undergoes further decomposition, it may form small molecular weight volatile by-products that do not form char and, in fact, may actually feed the combustion process. However, if after initial decomposition the polymer radical reacts with another polymer chain, the polymer may form a crosslinked char. This mechanism would help explain why the char of many highly aromatic polymers contain graphitic structures on the surface.

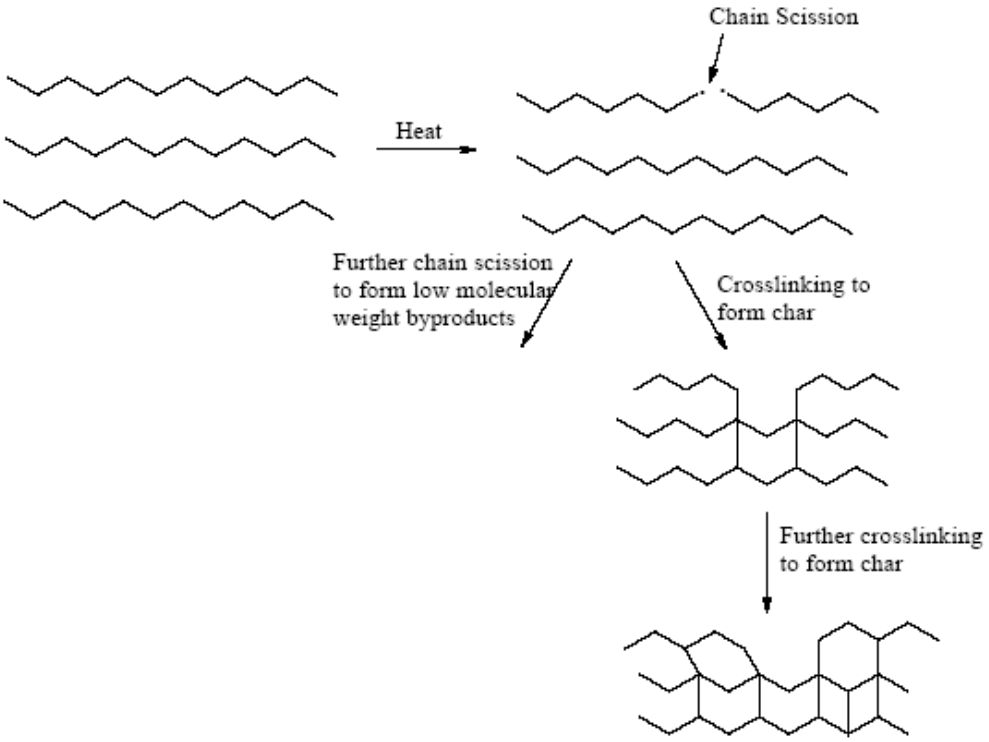
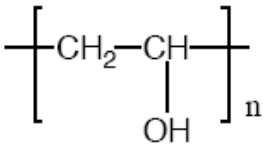
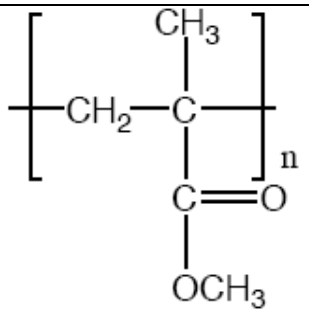
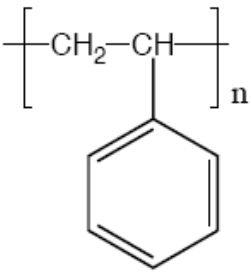
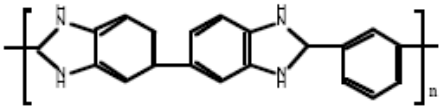
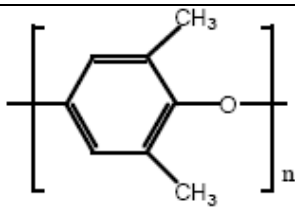
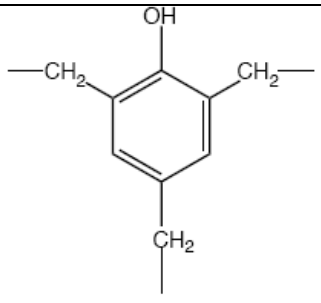


Figure 2.8 Possible mechanism for char formation

These char forming condensed phase reactions are important in fire resistant polymers, such as poly 2,6-dimethyl-1,4-phenylene oxide (PPO) and phenolic resins. Fenimore and Martin [10] illustrated that the high limiting oxygen index of PPO was due to its ability to form char residue upon heating. Table 2.3 illustrates the effect of aromatic rings upon char formation in non-halogenated polymers [10]. It is evident from this data that as the char yield increases, so does the LOI.

Table 2.3 Effect of Aromatic Rings upon the Char Yield

Polymer	**Structure**	**Oxygen Index**	**Char Yield**
Poly(vinyl alcohol)		22	0
Poly(methyl Methacrylate)		17	0
Polystyrene		18	0
Poly(benzimidazole)		-	58
Poly(phenylene oxide)		28	40
Phenolic Resin		35	60

2.3 Controlled/ “Living” Radical Polymerization (CRP)

The development of new polymeric materials is based on the availability of methods, pricipally living polymerizations [2].

Clearly the field of CRP has developed since the seminal paper on SFRP of styrene by Georges in 1993 [27]. There are several approaches to controlling free radical polymerization by suppressing the contribution of chain breaking reactions and assuring quantitative initiation [28]. All of these approaches employ dynamic equilibration between growing free radicals and varius types of dormant species. These reactions are described as controlled radical polymerizations (CRP) or controlled/living radical polymerizations rather than as true living radical polymerizations, due to the presence of unavoidable termination, which is intrinsically incompatible with the concept of living polymerizations [29].

In the past decade, limitations of FRP have been overcome as several procedures for CRP have evolved based on an understanding and integration of chemistry developed the past 60 years in the fields of organic chemistry, conventional radical polymerization, and living ionic polymerizations (Figure 2.9).

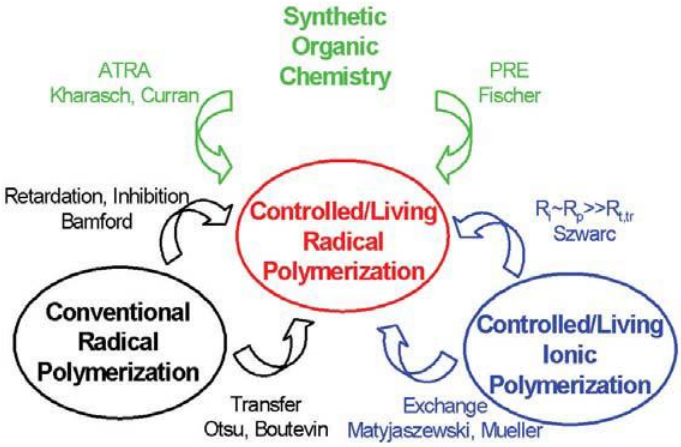


Figure 2.9 Development of CRP by integration of advances in several fields of chemistry.

Living polymerizations are chain-growth polymerizations that proceed in the absence of irreversible chain transfer and chain termination [2].

There are two caveats for living radical polymerizations. The first is that irreversible termination is only minimized in these polymerizations and not excluded from the mechanism. Therefore, these polymerizations do not meet the strict definition of a living polymerization and are more properly termed controlled/living polymerizations to reflect the uncertainty regarding the contribution of unavoidable irreversible termination. Second, above some molecular weight value specific to the polymerization of each monomer, all controlled/ "living" radical polymerizations can no longer be considered controlled, because slower termination, transfer and other side reactions become significant [2]

2.3.1 Classification of CRP

It is possible to group CRPs into several categories, depending on the chemistry of exchange and structure of dormant species. Mechanistically, CRPs can be classified into four different cases [30].

a) *Case 1* is best exemplified by nitroxide mediated polymerization in the presence of TEMPO, and bulky acyclic nitroxides, triazolinyl radicals, some bulky organic radicals, e.g. trityl , photolabile C-S bonds and organometallic species [30].

b) *Case 2* is a subset of Case 1, since it is based on the catalyzed, reversible cleavage of the covalent bond in the dormant species via a redox process. Because the key step in controlling the polymerization is atom (or group) transfer between growing chains and a catalyst, this process was named atom transfer radical polymerization (ATRP) and is catalyzed by various Ru, Cu, Fe and other transition metal derivatives [30].

c) *Case 3* has not yet been as successful as the above two systems. This process involves the reversible formation of persistent radicals (PR) by reaction of the growing radicals with a species containing an even number of electrons. PRs do not react with each other or with monomer.

d) *Case 4* is based on a thermodynamically neutral exchange process between a growing radical, present at very low concentrations, and dormant species, present at

much higher concentrations. This degenerative transfer process can employ alkyl iodides, unsaturated metacrylate esters , or thioesters [30].

The only difference between the first two cases is the bimolecular activation and catalyzed nature of the second system. Also, case 4 is very different from the other three. There is no persistant radical in it.

2.3.2 Basic requirements for CRP

The most important difference between conventional and controlled/ "living" radical polymerizations is the lifetime of an average chain. In conventional systems chain is born, grows and dies within approximately 1s; during this time it is not possible to perform any synthetic manipulations such as chain extension, end functionalization, variation of monomer feed etc. On the other hand, under controlled/ "living" conditions, chains grow during several hours anabling precise macromolecular engineering. Long lifetime of chains requires sufficiently low concentrations of macroradicals but also sufficiently high concentration of propagating chains. This can be accomplished via equilibration between active free radicals and various dormant species [30].

There are three general requirements for CRP [28].

- Fast exchange between dormant species and growing radicals
- A small proportion of chains involved in chain breaking reactions
- Fast and quantitative initiation.

One of the most important parameters is the number of monomer molecules added to the growing chain during one activation step. If this number is very low, preferentially less than unity, then polymers with low polydispersities and good control of molecular weights are obtained. If this number is very large, exceeding the targeted degree of polymerization, then poor control is obtained and the polymerization may resemble a conventional, thermally or redox initiated system [30].

In all controlled and conventional radical polymerization systems termination does occur. In the first approximation, the concentration of terminated chains depends only on polymerization rate. However, the ratio of the concentrations of terminated chains to the sum of the active and dormant chain concentrations can be dramatically different in both systems. In conventional radical polymerization, nearly all chains are terminated. In controlled systems, the proportion of terminated chains can be very small, usually less then 10%. It is important to know precisely the proportion of these chains since they can not be functionalize or extended in the form of block copolymers, etc [30].

Some attributes of controlled/ "living" radical polymerizations include the linear evolution of molecular weights with conversion, and the formation of polymers with low polydispersities and high degrees of end functionality as well as efficient block copolymerization. All of these features require quantitative initiation. In CRP systems this is translated into a constant or nearly contant number of growing chains. In NMP and ATRP, it is necessary to select an initiator which resembles the structure of dormant chains or has somewhat higher intrinsic reactivity. If the initiator generates too many radicals, termination may reduce its efficiency [30].

2.3.3 Applications

A number of CRP methods have been developed and the three most promising are: stable free radical polymerization (SFRP), most commonly nitroxide mediated polymerization (NMP) but may also include organometallic species (Fig.2.10, scheme 1); transition-metal-catalyzed atom transfer radical polymerization (ATRP) (Fig.2.10, scheme 2); and degenerative transfer with alkyl iodides, methacrylate macromonomers, and dithioesters via reversible addition-fragmentation chain transfer (RAFT) polymerization (Fig.2.10, scheme 3)[31].

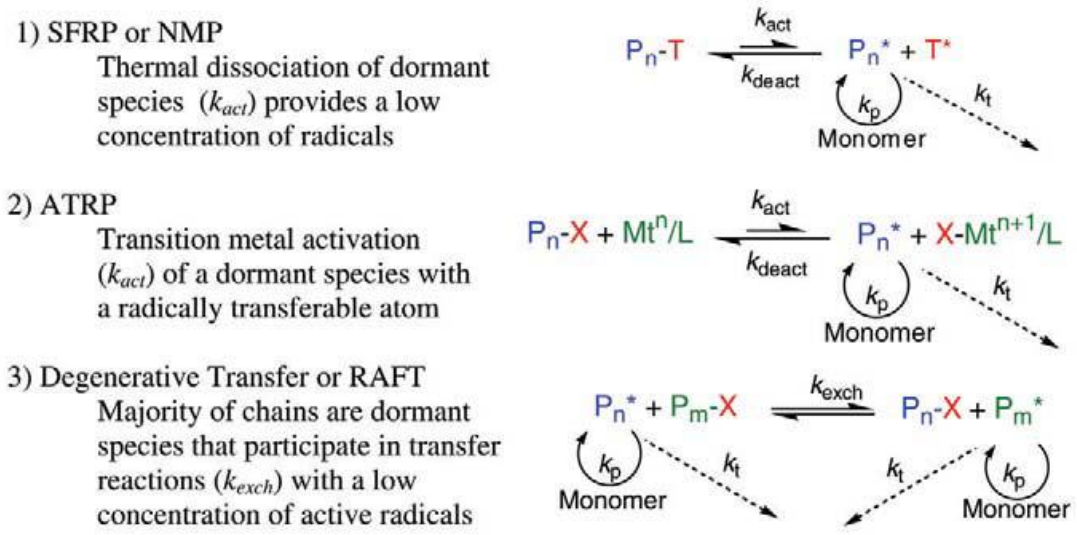


Figure 2.10 The three main CRP methods.

2.3.3.1 Nitroxide Mediated Polymerization (NMP)

NMP was originally best represented by TEMPO. TEMPO could be successfully applied only to styrene and copolymers due to its relatively small equilibrium constant. For acrylates and metacrylates it yields either unsaturated oligomers/polymers or poorly controlled polymers. When TEMPO is used for NMP reactions are carried out in bulk and at high temperatures(>120°C) because they are inherently slow, although some acceleration was described in the presence of sugars, acyl compounds and acids. Polymerizations in solution, dispersion and emulsion have been also reported. As initiators, either a combination of conventional initiator (AIBN) and free nitroxide or performed alkoxyamines can be used. End groups in the dormant species are alkoxyamines and some unsaturated species formed by abstraction of β-H atoms or other inactive groups formed by side reactions, e.g, termination [30].

In general mechanism (Figure 2.11), the reversible termination of growing polymeric chain is the key step for reducing the overall concentration of the propagating radical chain end.

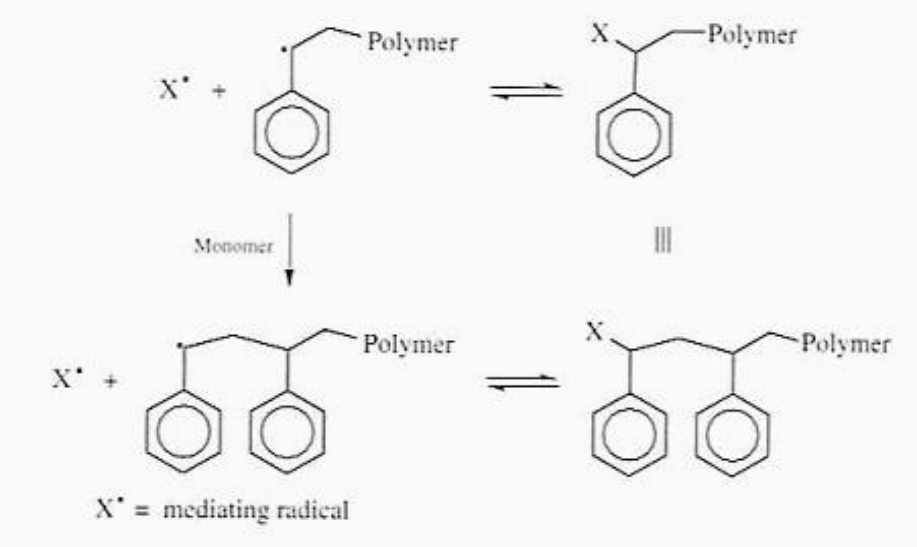


Figure 2.11 The general outline of living free-radical mechanism

2.3.3.2 Reversible-Addition-Fragmantation Chain Transfer Process (RAFT)

RAFT is a special case of degenerative transfer. Reversible addition-fragmentation chain transfer (RAFT) can be potentially used for any radically polymerizable monomer. In principle, all classic radical systems can be converted to RAFT or to another degenerative transfer systems in the presence of efficient transfer reagents. The end groups are either alkyl iodides, methacrylates or thioesters. No catalyst is needed for degenerative transfer but, in fact, the role of the catalyst is played by the radical initiator. This also means that the initiator may incorporate some undesired end groups and the amount of termination is governed by the amount of the decomposed initiator. A potential disadvantage of degenerative transfer is that there is always a low molecular weight radical available for termination [30]. The products, whether homopolymers, random copolymers, gradient, or block copolymers, are of controlled molecular weight and generally have very narrow polydispersities (usually PDI<1.2, and sometimes <1.1) [32].

2.3.3.3 Atom Transfer Radical Polymerization (ATRP)

As a novel precision polymerization, atom transfer radical polymerization (ATRP) has received rapidly increased interest recently, since it furnishes control over the resulting polymers, which posses narrower molecular weight distributions.The merit of the ATRP system is that it can be performed by an ordinary polymerization

procedure[33]. The name atom transfer radical polmerization (ATRP) comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of polymeric chains. ATRP originates in atom transfer radical addition (ATRA) reactions [34]. It employs atom transfer from an organic halide to a transition- metal complex to generate the reacting radicals, followed by back transfer from the transition metal to a product radical to form the final product [2]. The general mechanism of ATRA can be seen in Figure 2.12.

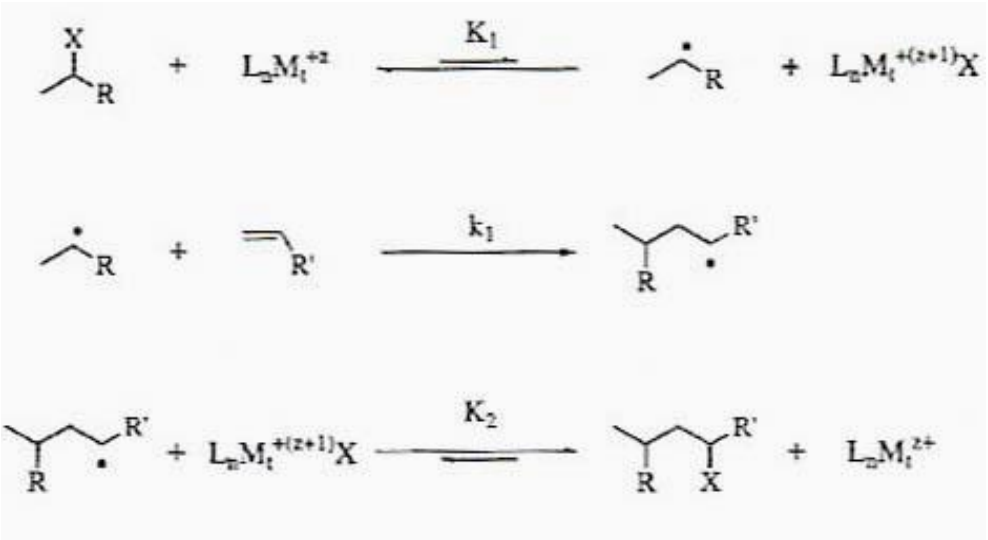


Figure 2.12 The general mechanism of ATRA

- **Mechanism and Kinetics of ATRP**

ATRP was developed by desining a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process. [35, 36, 37].

This allowed for an unprecedented control over the chain topology, the composition and the end functionality (Figure 2.13) for a large range of radically polymerizable monomers .

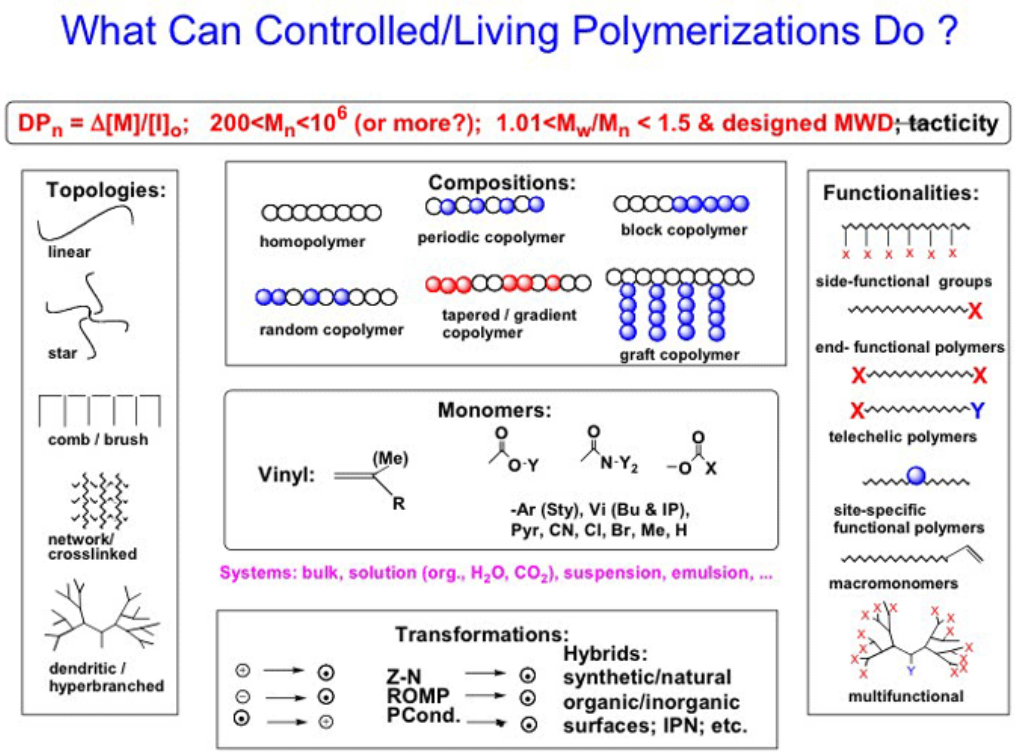


Figure 2.13 A schematic represantation of new polymers and materials prepared by using ATRP

A general mechanism for ATRP is shown in Figure 2.14. In ATRP technique, the halide (X) atom is produced from an activation of alkyl halide, the alkyl halide also producing an alkyl radical initiator. This reaction is catalyzed by a complex formed between a transition metal compound such as CuBr or CuCl and ligands [38].

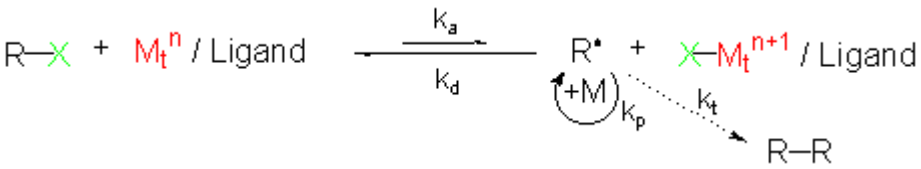


Figure 2.14 A general mechanism for ATRP

This process occurs with a rate constant of activation, k_a, and deactivation k_d, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to conventional radical polymerizations, with the rate constant of propagation, k_p.

Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.
Higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control may be observed at higher temperatures.

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator (CuX_2 / Ligand).

The rate law of ATRP is formulated in discussed conditions and given in equation (2.1) [39].

$$R_p = k_{app}[M] = k_p[P^{\cdot}][M] = k_p K_{eq}[I]_0 \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.1)$$

- **Molecular weight and Molecular weight distribution**

As in typical living polymerization, the average molecular weight of the polymer can be predetermined by the ratio of consumed monomer and the initiator ($DP_n=\Delta[M]/[I_0]$) while maintaining a relatively narrow molecular weight distribution ($1.0<M_w/M_n<1.5$) [40]. In addition, precise contol over the chemistry and the structure of the initiator and active end group allows for the synthesis of end-functionalized polymers and block copolymers.

The molecular weight distribution or polydispersity M_w/M_n is the index of the polymer chain-length distribution. In well-controlled polymerizaiton, M_w/M_n is usually less than 1.10. [39]

- **Components used in ATRP**

a) Monomers

ATRP can be used for many vinyl monomers including styrenes, acrylates methacrylates, acrylonitrile and dienes. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq}=k_a/k_d$) determines the polymerization rate [39].

The values of the equilibrium constants are lower for monosubstitued alkenes than for disubstitued alkenes (MMA>MA). The equilibrium constan decreases in the following order with α-substituents: CN>Ph>C(O)OR>C(O)NR_2>COC(O)R [40].

The most commonly used monomers are styrene(St) and methylmetacrylate (MMA) and acrylates.

Styrene

ATRP of styrene and its derivatives has been reported for the copper, iron, ruthenium, and ruthenium catalytic systems, with the majority of the work performed using copper-based systems. Non-polar solvents are recommended for styrene ATRP [2].

Polystyrenes can be prepared within the molecular weight range of 1000 to 90000.
In the region from 1000 to 30000 the polydispersities fall within the range of 1.10 to 1.50 [2].

Acrylates

The controlled ATRP of acrylates has been reported for copper, ruthenium and iron based systems [2]. Well-defined polyacrylates with M_n up to 100000 and $M_w/M_n<1.1$

can be prepared. Depending on the catalyst, a wide range of polymerization temperatures are possible to produce polymers within a reasonable time.

Methyl Methacrylate

The controlled polymerization of methacrylates to polymers of specific architecture, with a range of designed properties/effects, is of continuing widespread interest [41]. ATRP of MMA has been reported for the copper, ruthenium/aluminum alkoxide, iron, and nickel catalyst sytems [2]. The best initiators for MMA ATRP are p-toluenesulfonyl chloride, benzhydryl chloride, and dialkyl 2-bromo-2-methylmalonates. Well-defined poly(methylmethacrylate) can be prepared within the molecular weight range of 1000 to 180000, and analogy to acrylate esters, potentially a wide variety of methacrylate esters can be polymerized using ATRP. The ranges within which the resulting polymer retains narrow molecular weight distribution ($M_w/M_n < 1.5$) varies between catalyst systems [2].

b) Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

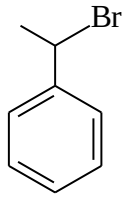
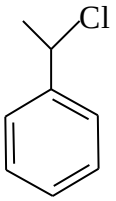
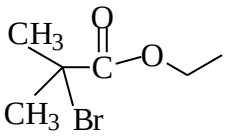
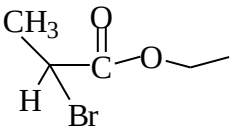
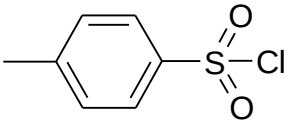
In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best [2]. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage[39].

Initiation should be fast and quantitative with a good initiator and proper selection of group R. Any alkyl halide with activating subtitunets on the α-carbon, such as aryl carbonyl, or allyl groups, can potentially be used as ATRP initiators,

polyhalogeneted compounds (CCl_4 and $CHCl_3$), and compounds with a week R-X bond, such as N-X, S-X and O-X, can also be used as ATRP initiators.

When the initiating moiety is attached to a macromolecule macroinitiators are formed, and can be used to synthesize block or graft copolymers [42].

Table 2.4 The most frequently used initiator types in ATRP systems

Initiator	**Monomer**
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methylmethacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

c) Catalysts

Perhaps most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of

exchange between the dormant and active species [39]. The catalyst is based on a transition metal which regulates the polymerization rate and polydispersities [30]. There are several prequisites for an efficient transition metal catalyst.

a) The metal center must have at least two readily accesible oxidation states seperated by one electron

b) The metal center should have reasonable affinity toward a halogen.

c) The coordination sphere around the metal should be expandble on oxidation to selectively accomodate a (pseudo) halogen.

d) The ligand should complex the metal relatively strongly.

e) The position and dynamics of the ATRP equilibrium should be appropriate for the partical system [39].

d)Ligands

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First, fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third, fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth, relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals [39].

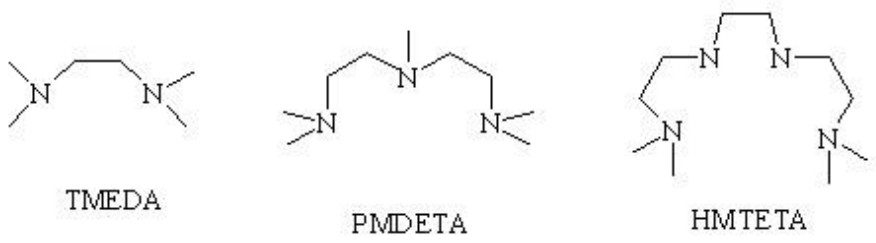


Figure 2.15 Nitrogen based ligands

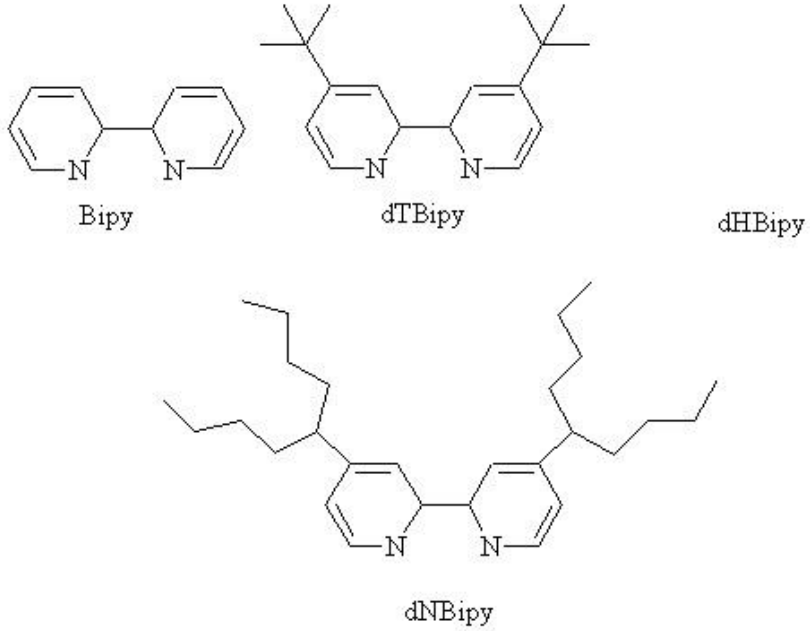


Figure 2.16 Derivatives of 2,2-bipyridine

e) Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g.,emulsion,suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether,ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, DMSO [43] and many others have been used for different monomers. Solvents are often used to reduce viscosity at high conversion chain transfer to solvent should be minimal[39].

f) Deactivator

The deactivator in ATRP is higher oxidation state metal complex formed after atom transfer, and it plays a vital role in ATRP in reducing the polymerization rate and the polydispersity of the final polymer.

In ATRP the concentration of deactivator increases sharply at the beginning of the polymerization and then increases slowly, but continiously, with monomer conversion [44].

Table 2.5 Comparison of NMP, ATRP and Degenertive Transfer Systems

Feature	**Systems**		
	NMP	**ATRP**	**RAFT**
Monomers	-styrenes for TEMPO -also acrylates and acrylamides for new nitroxide -NO metacrylates	-nearly all monomers with activated double bonds -NO vinyl acetate	-nearly all monomers
Conditions	-elevated temp. (>120 °C for TEMPO) -water-borne systems -sensitive to O_2	-large range of temp. (-30 to 150 °C) -water-borne systems -tolerance to O_2	- elevated temp. For less reactive monomers -water-borne systems -sensitive to O_2
End Groups	*Alkoxyamines* -thermally unstable	*Alkyl (pseudo)halides* -thermally and photostable	*Dioesters, iodides and metacrylates* -thermally and photo less stable
Additives	None	Transition metal catalyst -shoul be removed	Conventional radical initiator -may decrease end functionality -may produce too many new chains

Among this techniques, ATRP seems to be most effective system, due to being able to polymerize a variety of monomers and giving a relatively low polydispersity polymers [45]. Table 2.5 summerizes the main features of three discussed systems.

Light-induced free radical polymerization is of enormous commercial importance. Techniques such as curing of coatings on wood, metal and paper, adhesives, printing inks, and photoresists are based on photoinitiated radical polymeriation.

e)Temperature and Reaction Time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant [39]. The energy of activation for radical propagation is appreciably higher than that for termination be radical combination and disproportionation. Consequently, at higher temperatures the ratio k_p/k_t will be higher and therefore better polymerization control will be observed [2].

The most important effect of reaction time in ATRP occurs at high conversions. At high monomer conversions, the rate of propagation is very slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent [39].

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Purification of Materials

3.1.1.1. Monomers

Styrene (St) (Fluka)

Washed with aq. 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure (50^0C / 25 mmHg). Middle fraction was collected and immediately used.

Methylmethacrylate (MMA) (Fluka)

Washed with aq. 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure .

3.1.1.2. Solvents

Tetrahydrofuran (THF) (J.T.Baker)

Dried and distilled over CaH_2, then it was let mixing over sodium/benzophenon ketyl, and was distilled prior to use.

Chloroform (Lab Scan)

Shaken with several portions of conc. H_2SO_4 washed throughly with water and dried with $CaCl_2$ before filtering and distilling (61^0C / 760 mmHg).

Dimethyl sulphoxide (Lab Scan)

Dried and distilled over CaH_2, then it was let mixing over sodium/benzophenon ketyl, and was distilled prior to use.

Methanol (Lab Scan)

It was used without further purification.

3.1.1.3. Other Chemicals and Reagents

p-Bromofluorobenzene (Acros)

It was used without further purification.

Dichlorophenyl phosphine oxide (Merck)

It was used without further purification.

Magnesium (Riedel-de Haen)

It was used without further purification.

Ethylene carbonate (Riedel-de Haen)

It was used without further purification.

Sodium carbonate (Merck)

It was used without further purification.

Potassium Hydroxide (Merck)

It was used without further purification.

Triethylamine (TEA) (Acros)

It was used without further purification.

2 – Bromopropionyl Bromide (Aldrich)

It was used without further purification.

Copper (I) Bromide (Aldrich)

It was used without further purification.

3.2. Equipments

3.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

H-NMR analysis were recorded on a Bruker 250 MHz Spectrometer.

3.2.2. Gel Permeation Chromatography (GPC)

GPC analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and four Waters Styragel Columns (HR 5E, HR 4E, HR 3, and HR2). THF was used as the eluent at a flow rate of 0,3 ml/min at 30^0C. The molecular weights of the polymers were calculated with the aid of polystyrene and polyMMA standards.

3.2.3. Differential Scanning Calorimeter (DSC)

The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (TA DSC Q10) in a flowing nitrogen atmosphere at heating rate 10^0C / min.

3.2.4. Thermogravimetrical Analysis (TGA)

Thermal gravimetrical analysis was performed on a TA TGA Q50 instrument.

3.2.5. Ultra-Violet Spectrophotometer (UV)

The UV spectra of products were determined by Pharmaspec UV-1700 Shimadzu spectrophotometer.

3.2.6. Infrared Spectroscopy

Infrared spectra were recorded on Schimadzu 8300 spectrophotometer.

3.3. Synthesis of Chemical Compounds

3.3.1 Synthesis of Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO)

Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO) was prepared by a variation of known Grignard techniques. A flame dried 2l 3-neck round bottom flask fitted with an overhead mechanical stirrer, an addition funnel and a nitrogen inlet were added 13,44 g (0,56 mol) magnesium and 600 ml dry THF. This solution was cooled with an ice water bath. To this stirred solution was added dropwise at or below 5 ^{0}C 98 g (0,56 mol, 61,51 ml) p-bromofluorobenzene over 2 hours. This mixture was stirred at room temperature overnight to give a gray slightly cloudy solution. Next, 40 ml (55,2 g, 0,28 mol) dichlorophenyl phosphine oxide was added dropwise at 5 ^{0}C over 2

hours and this solution was allowed to stir at room temperature overnight to give a yellow clear solution. Enough 10% aqueous sulfuric acid was added to make the solution acidic and water was added, yielding a homogeneous golden yellow mixture. Ether was added in order to seperate the solution into organic and aqueous phases. The aqueous layer was washed well with ether and all organic layers were combined. This organic solution was washed well with 10% sodium bicarbonate, followed by water washings. Then sodium sulphate was added to stir at room temperature overnight to clearing the cloudy ether phase. After filtering from the blue banded filter paper, THF and ether was distilled by rotary evaporator. Proportion of (30/70) of THF/hexane solution was used for crystallization. The crystals typically giving overall yields around 65% of monomer grade material with melting point of 126-127 ^{0}C [26].

3.3.2. Synthesis of Bis(4-hydroxyphenyl)phenyl phosphine oxide (BOHPPO)

BOHPPO was synthesized by hydrolyzing BFPPO using potassium hydroxide in DMSO. For example, 20 g (0,064 mol) BFPPO and 80 ml of DMSO were added to a 2 l 3-neck flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a condenser. To the solution was added a 15 N (21.3 ml) solution of 17,92g (0,32 mol) of potassium hydroxide in water. The solution was then raised to reflux (approximately 135 ^{0}C) and allowed to react for 8 hours. The solution was acidified well with 10% HCl and DMSO removed using a rotovap to afford a pale yellow solid. Water was then added to solid to remove remaining salt. The product was filtered, dried in vacum oven at 150 ^{0}C overnight, and then purified using fractional recrystallization from 1:5 v/v ratio of methanol/water. Then resulting material was considered to be monomer grade with a melting point of 236-237 ^{0}C. The yield of the reaction was 65% after purification [10].

3.3.3 Synthesis of Bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide (BOHEPPO)

A spherical flask (500 ml), equipped with a reflux condenser, stirrer, thermometer, and nitrogen inlet, was charged with 5g BOHPPO (0,016 mol), 2.816g ethylene carbonate (0,032 mol), and 0,016g sodium carbonate as catalyst. The mixture was

heated to 165-170 ^{0}C under nitrogen for 2 h. The crude product was washed with water several times to remove unreacted ethylene carbonate. A light brown viscose liquid was obtained. The yield of the reaction was 90% after purification [46].

3.3.4. Preparation of Bis [(4-β-(2-bromopropanoate)ethoxy)phenyl] phenyl phosphine oxide (BBEPPO)

Under nitrogen 1,7 ml (0.0162 mol) 2-bromopropionyl bromide was added dropwise to a stirring mixture of 2g bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide (BOHEPPO) **(**0.0054 mol) and 2,3 ml triethylamine (0.00162 mol) in 20 ml of $CHCl_3$ in an ice bath for 1 hour. After complete addition of the acid bromide, the reaction was stirred at room temperature for 1 hour. The reaction mixture was washed with water (3×20 ml) and then dried overnight with $MgSO_4$. After filtration and evaporation of $CHCl_3$ gave a sticky light brown, very viscose product. It was dried under oven at 40 ^{0}C and recrystallized from methanole twice (yield 58 %) [47].

3.3.5 General Polymerization Procedure for ATRP of Styrene (PSt)

To a schlenk tube equippped with magnetic stirrer, vacuum and dry nitrogen was applied 3 times, then 1,7 ml styrene, 0,021g copper(I)bromide, 62 μl ligand (PMDETA), and initiator 0,1 g BBEPPO were added under nitrogen respectively. 1.5 ml DMSO was used as solvent [43]. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostate at 57 ^{0}C. The polymerization was performed for 4, 8, 18 hours and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The filtrate was dried under vacuum. The conversion was determined gravimetrically. ATRP conditions and results are given in Table 4.1

3.3.6 General Polymerization Procedure for ATRP of Methyl methacrylate (PMMA)

To a schlenk tube equippped with magnetic stirrer, vacuum and dry nitrogen was applied 3 times, then 1,6 ml methyl methacrylate, 0,021g copper(I)bromide, 62 μl ligand (PMDETA), and initiator 0,1 g BBEPPO were added under nitrogen respectively. 1.5 ml DMSO was used as solvent [43]. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostate at 57 ^{0}C. The polymerization was performed for 4, 8, 18 hours and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The filtrate was dried under vacuum. The conversion was determined gravimetrically. ATRP conditions and results are given in Table 4.2

4. RESULTS AND DISCUSSION

In this thesis, difunctional initiator was prepared by esterification of Bis [(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide compound with 2-bromopropionyl bromide. It was used to initiate atom transfer radical polymerization of the styrene and methyl methacrylate. Consequently, PSt and PMMA homopolymers possessing two reactive bromine end groups in the main chain was obtained.

4.1 Synthesis of Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO)

In this part, BFPPO was synthesized according to the procedure [26] in Figure 4.1. The structure of product was confirmed by FT-IR spectrum.

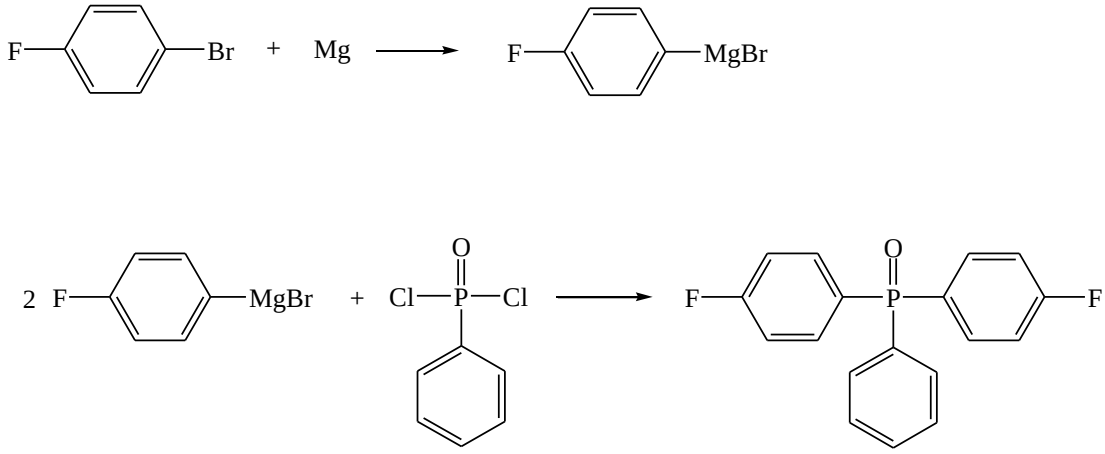


Figure 4.1 Synthesis scheme of BFPPO

The FT-IR spectrum of BFPPO in Figure 4.2 contains the characteristic broad band (P=O) ν = 1394 cm^{-1}, (P-Ph) ν = 1434 cm^{-1}, (C-F) ν = 1220 cm^{-1}, (-CH) ν = 3057 cm^{-1}, and (C=C) ν = 1434-1589 cm^{-1}.

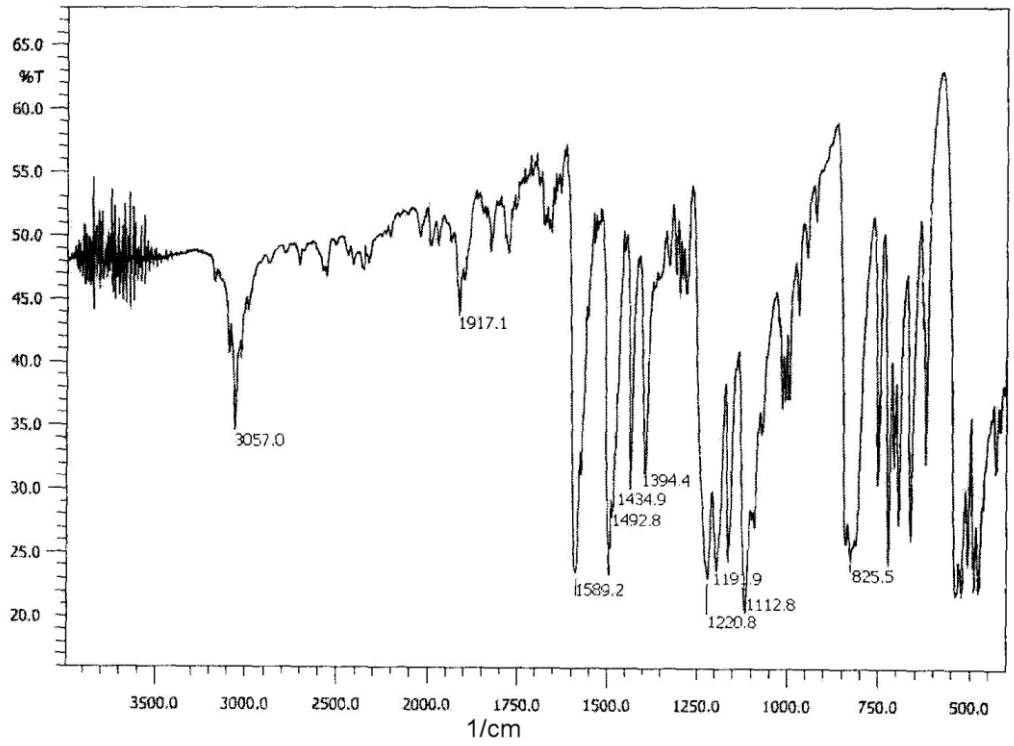


Figure 4.2 FT-IR spectra of BFPPO

4.2 Synthesis of Bis(4-hydroxyphenyl)phenyl phosphine oxide (BOHPPO)

In this part, BFPPO was synthesized according to the procedure [10] in Figure 4.3.

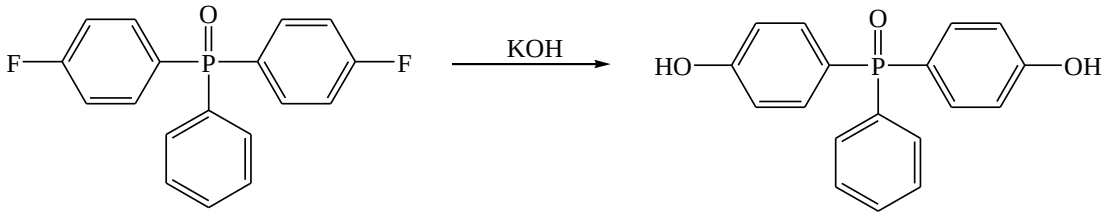


Figure 4.3 Synthesis scheme of BOHPPO

The chemical structures of the resulting material (BOHPPO) was characterized by FT-IR (Figure 4.4). The characteristic absorption peak of the functional group (Ph-OH) 3138 cm^{-1} was detected for BOHPPO. Peaks at 1278 cm^{-1} (-P=O), 1436 cm^{-1} (-P-Ph), 1122 cm^{-1} (C-O), and 1583-1600 cm^{-1} (C=C) proved the existence of phenyl phosphine oxide and hydroxy structure.

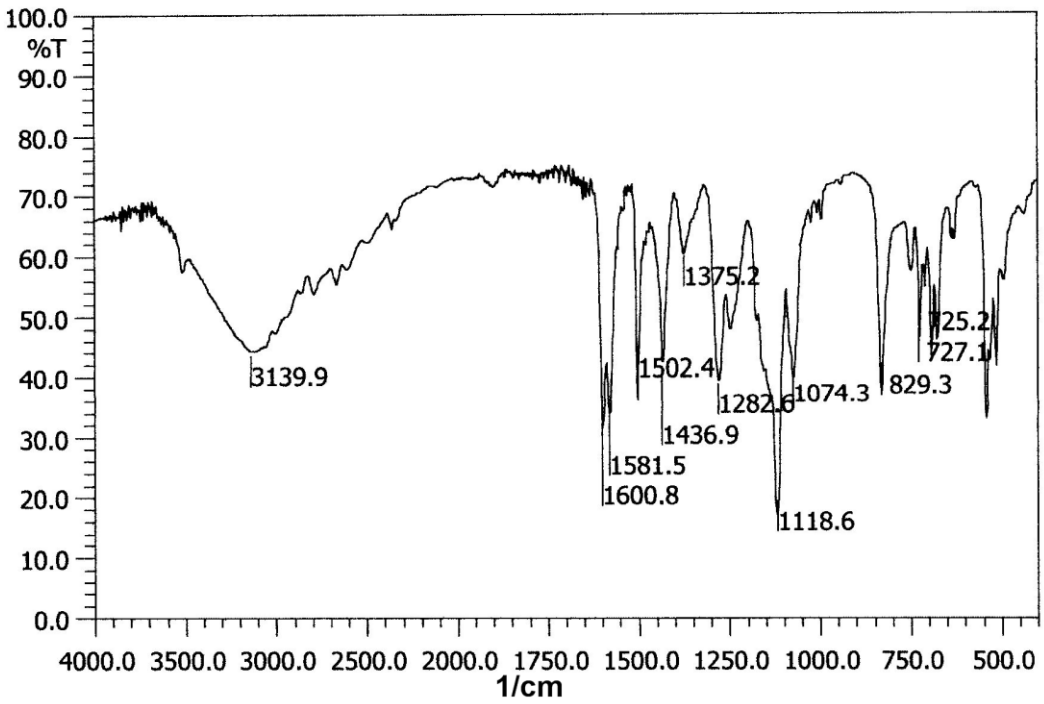


Figure 4.4 FT-IR Spectra of BOHPPO

4.3 Synthesis of Bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide (BOHEPPO)

In this part, BFPPO was synthesized according to the procedure [46] in Figure 4.5.

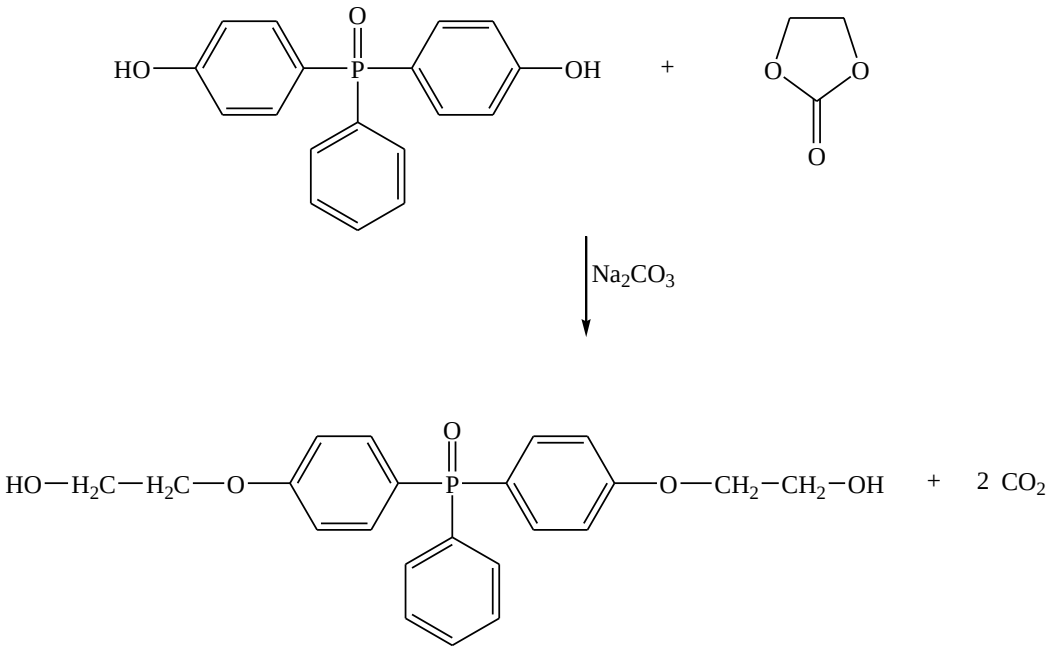


Figure 4.5 Synthesis scheme of BOHEPPO

The structure of BOHEPPO was confirmed by IR, ^{1}H-NMR, and UV spectroscopy, respectively.. Figure 4.6 presents the FT-IR spectra of BOHEPPO.

In the IR spectra, absorptions due to hydroxy groups was observed at 3302 (-CH_2-OH), 1162-1045 (-C-O), 2931-2872 (-CH), 1594-1500 (C=C), and an absorption based on triphenylphosphine was observed at 1436 cm^{-1}.

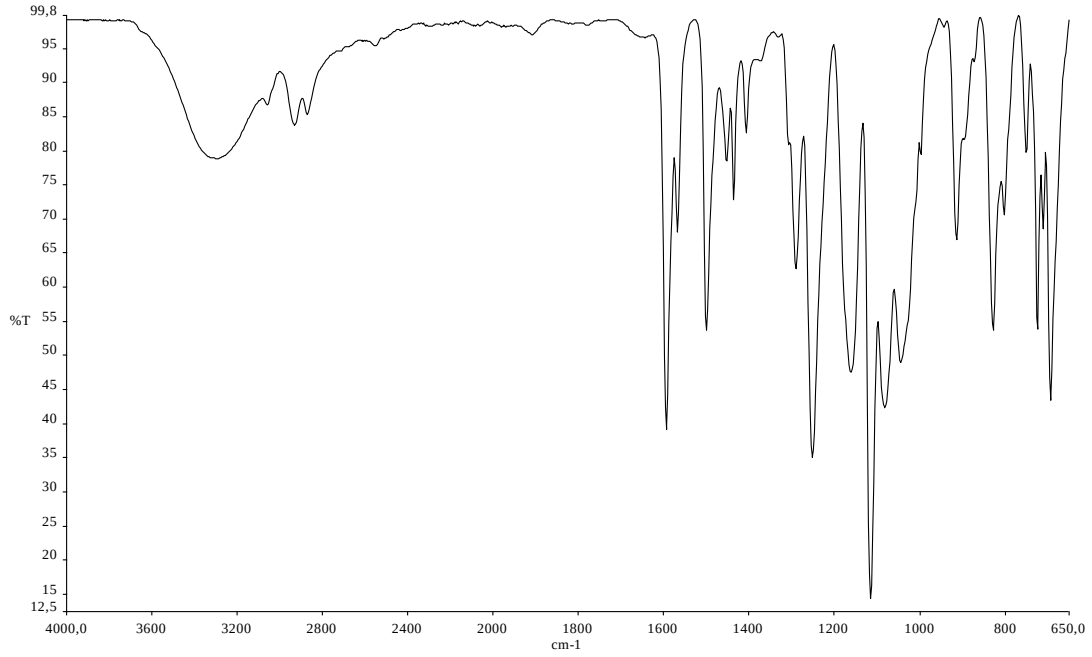


Figure 4.6 FT-IR spectra of BOHEPPO

The compound was further characterized by ^{1}H-NMR, as shown in Figure 4.7, measured with $CDCl_3$ as an external reference. Absorptions of characteristic aromatic protons were found at δ= 6,9-7,7 ppm, δ= 3,9-4,1 ppm (-OCH_2), and δ= 2,0-2,4 (-OH). We can also see the CH_2Cl_2 protons at δ= 5, ppm because of working hardness and rigidity of organic material. We add a very small amount of CH_2Cl_2 in it to use it easily.

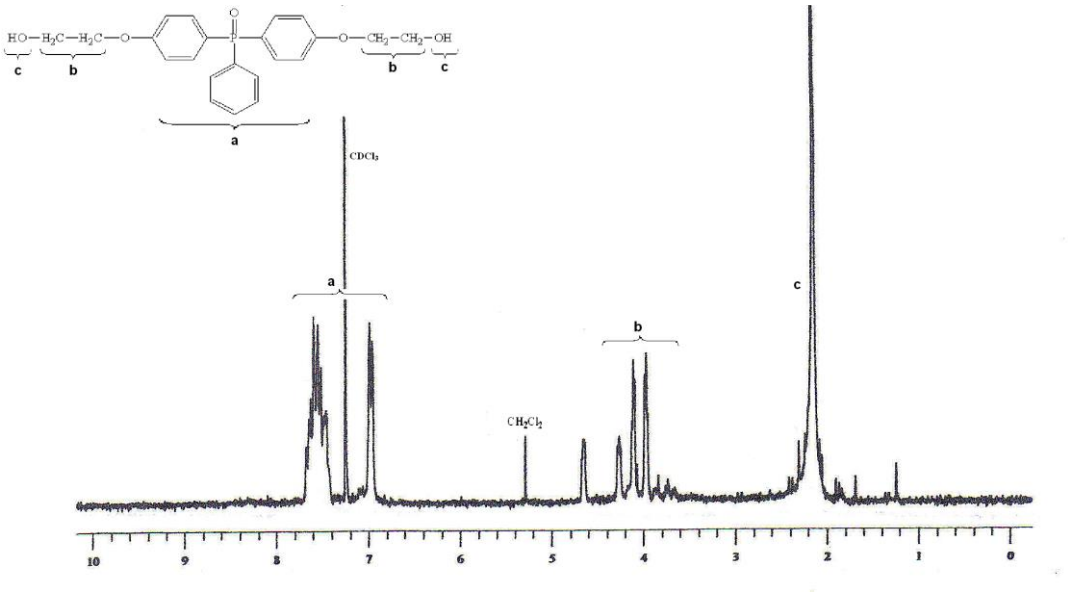


Figure 4.7 ^{1}H-NMR Spectrum of BOHEPPO

BOHEPPO is a photosensitive organic material containing aryl groups (chromophoric groups). BOHEPPO exhibited UV spectra corresponding to π-π^{*} transitions, as shown in Figure 4.8 showed absorption maxima at 244 and 282 nm.

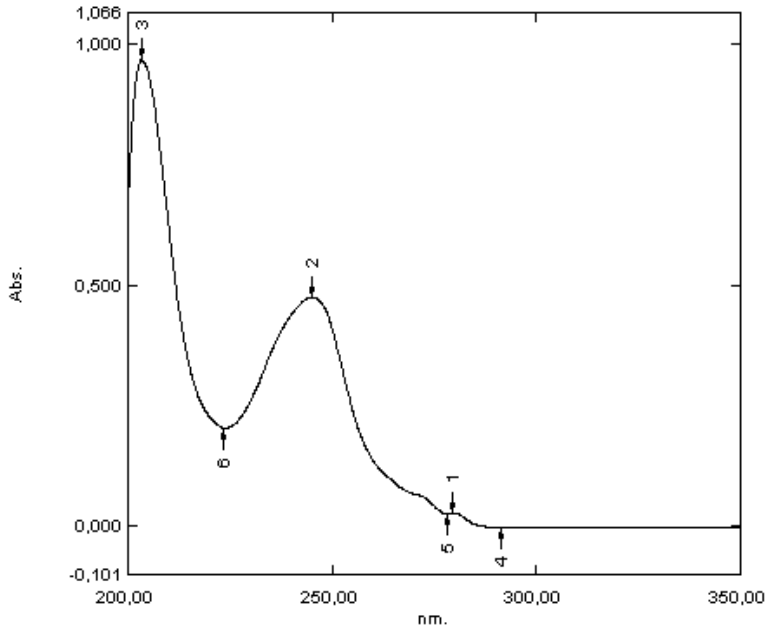


Figure 4.8 UV-Vis absorption spectrum of BOHEPPO in methanole

4.6 Preparation of Bis [(4-β-(2-bromopropanoate)ethoxy)phenyl] phenyl phosphine oxide (BBEPPO)

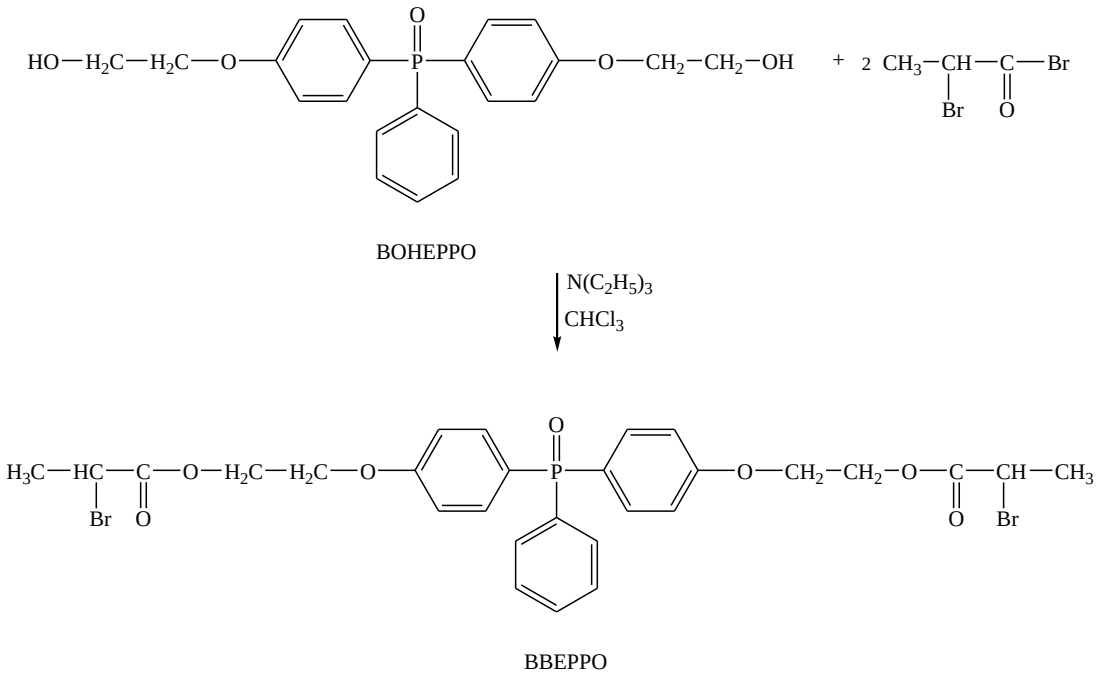


Figure 4.9 Synthesis scheme of BBEPPO

BBEPPO was synthesized according to the modified method of Paik et al.[47] (Figure 4.9). BBEPPO was prepared from esterification reaction of BOHEPPO and 2-bromopropionylbromide with 58 % yield.

A typical IR spectrum is shown in Figure 4.10. The FT-IR spectrum of BBEPPO exhibited characteristic absorption bands for the ester at 1736 (C=O), 1252 (P=O stretching vibration), 2928 (C-H stretching vibration), 1150-1067 (C-O stretching vibration), 1595-1501 (C=C stretching vibrations) and 1428 cm^{-1}(P-Ph stretching vibrations).

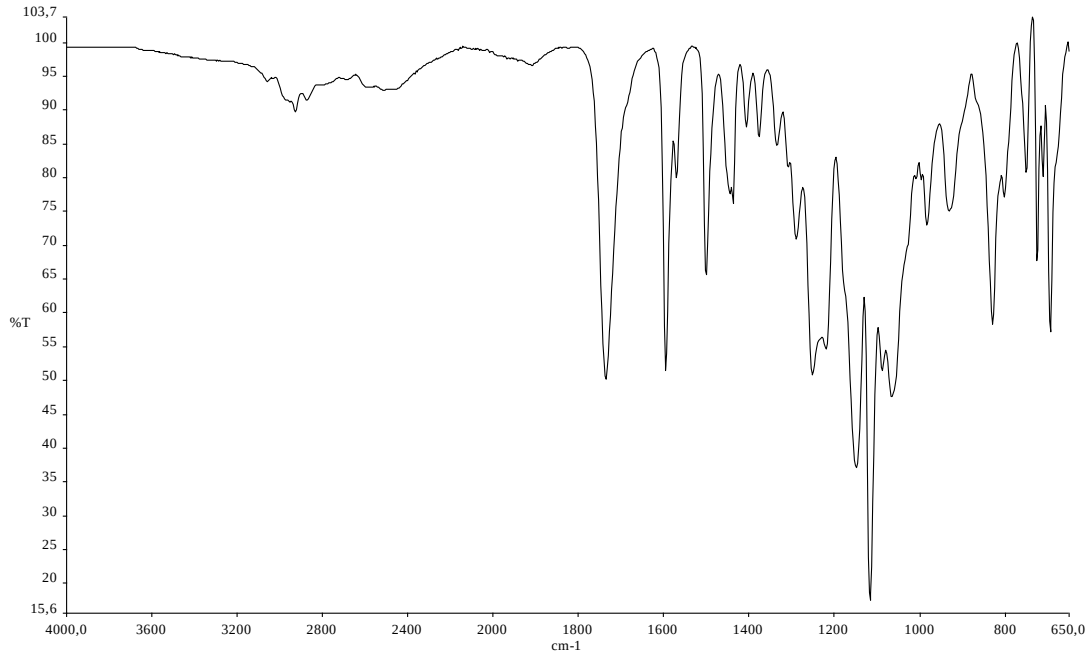


Figure 4.10 FT-IR spectra of BBEPPO

^{1}H-NMR spectrumof BBEPPO was taken in DMSO-d_6 as shown in Figure 4.11. The spectrum prove the expected structure of the macroinitiator BBEPPO. According to the spectrum, the signals originating from esterificated Br end group of BBEPPO were discerned at 1,6-1,7 ppm (-CH(Br)$\underline{CH_3}$), 4,2-4,7 ppm [(-$\underline{CH}$(Br)CH_3) and (-OCH_2)], and 7-7,6 ppm phenyl protons. We can see a typical methanole protons at δ= 3,1-3,8 ppm. After the crystallization of BBEPPO, we put the organic material into the oven at 40-50 ^{0}C. Bu we couldn't evaporate the methanole because of the sticky structure of phosphorus.

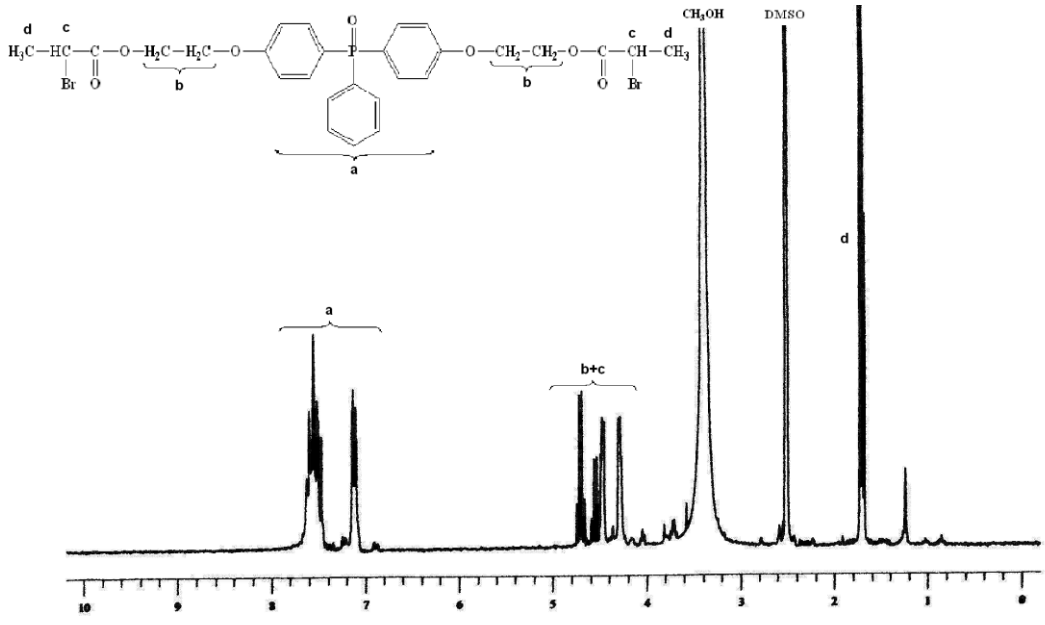


Figure 4.11 ^{1}H-NMR Spectrum of BBEPPO

The spectrum of BBEPPO was recorded at UV-Visible Spectrophotometer over the wavelength range 200-350 nm. As seen in Figure 4.12. The first and the second absorption bands were observed at λ= 282 and 244 nm in methanole, respectively.

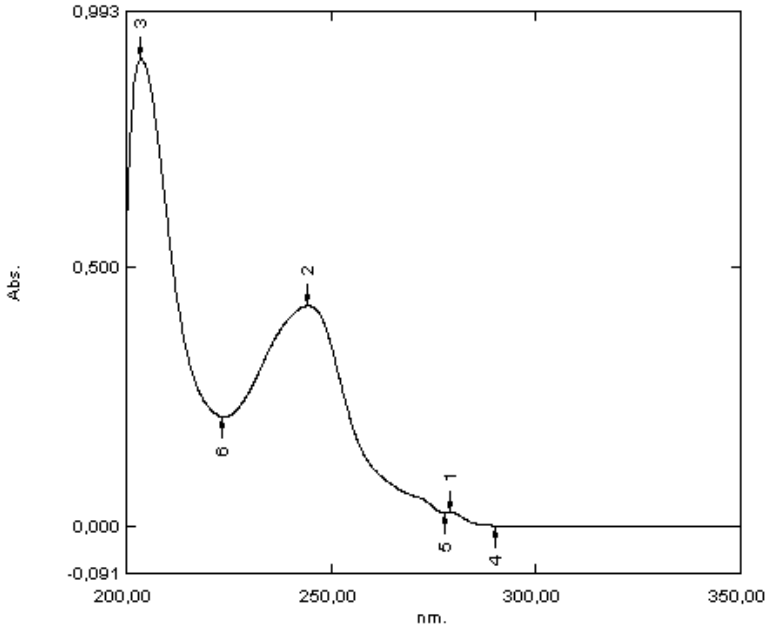


Figure 4.12 UV-Vis absorption spectrum of BBEPPO in methanole.

4.6 Preparation of Polystyrene (PSt) by ATRP mechanism using BBEPPO

Polystyrene homopolymer which has two functional bromine end groups was obtained via Atom Transfer Radical Polymerization with BBEPPO in the presence of a copper catalyst which has been shown in Figure 4.13.

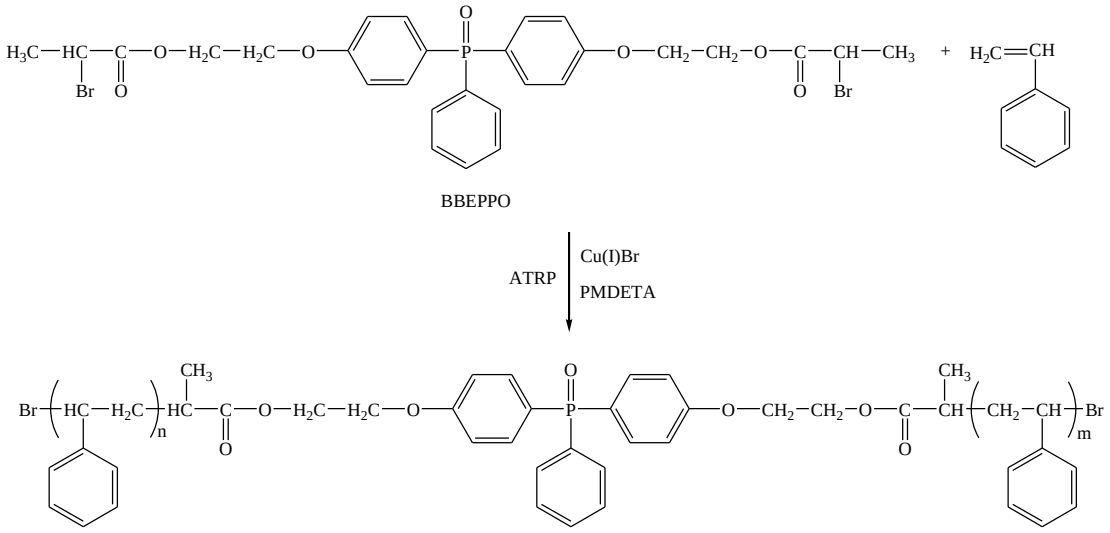


Figure 4.13 Synthesis scheme of PSt

The ^{1}H-NMR spectra of PSt's (Figure 4.14) were consistent with its chemical structure. The absortion of aromatic and (-CH_2-CH) protons at 6,5-7,3 ppm, 1,4-1,8 ppm, respectively. This observation suggests that we obtain PSt.

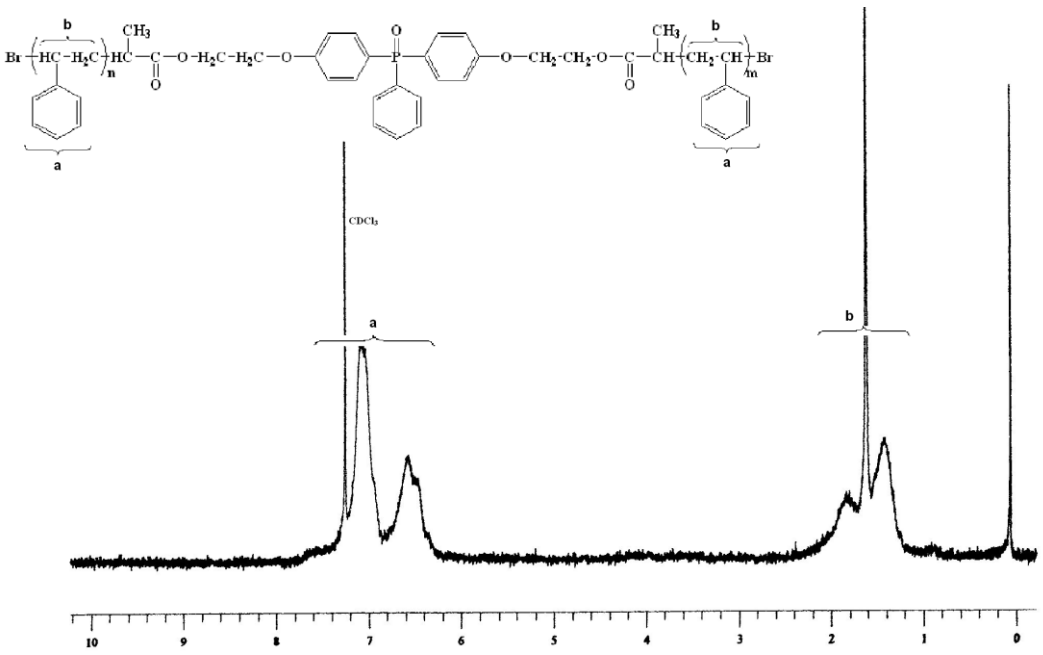


Figure 4.14 ^{1}H-NMR Spectrum of PSt

Figure 4.15 shows the absorption spectra of PSt. The spectra contains an absorption band characteristic of aryl group at λ= 282 and 244 nm, respectively.

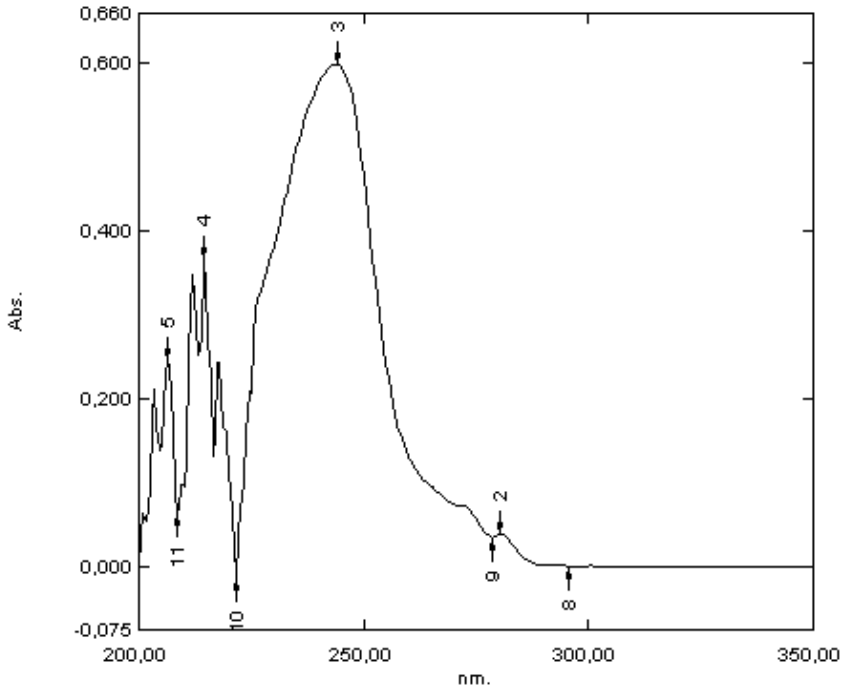


Figure 4.15 UV-Vis absorption spectrum of PSt in CH_2Cl_2.

Typical results concerning the polymerization of PSt in the presence of BBEPPO are presented in Table 4.1.

Table 4.1 ATRP of PSt bu using BBEPPO[a]

Run No	[BBEPPO][a] (mol/L)	[M_o] (mol/l)	$[I_o]^b/[Cu^+]/[PMDETA]/[M_o]^c$	Time (h)	Conv. (%)	M_n[d]	$M_{n(theo)}$[e]	M_w/M_n
PSt1	0,06	6	1/1/2/100	4	7	3400	774	1.18
PSt2	0,06	6	1/1/2/100	8	10	4100	1004	1.20
PSt3	0,06	6	1/1/2/100	18	20	9600	2041	1.11

[a]Temperature: 50 ^{0}C

[b]Initial initiator concentration

[c]Initial monomer concentration

[d]Determined by GPC based on PSt standarts

[e]Calculated by $[M_o]/[I_o] \times conv. \times M_{w\,(monomer)}$

Solvent : DMSO

The resulting polymers have molecular weights between 3400 to 9600 g/mol narrow polydispersities was observed from 1.20 to 1.11 and the theoritical molecular weights ($M_{n(theo)}$) were calculated according to following equation in each case.

$$[M_o]/[I_o] \times conv. \times M_{w\,(monomer)}$$

where $[M_o]$ and $[I_o]$ are the initial molar concentrations of the monomer and initiator, respectively and M_w is the molecular weight of the monomer [48].

The theoritical molecular weights of the resulting polymers was higher than the GPC values. This could be explained by the differences between polystyrene standarts.

The narrow molecular weight distributions were also obtained for PSt1, PSt2, and PSt3 as shown in Figure 4.16.

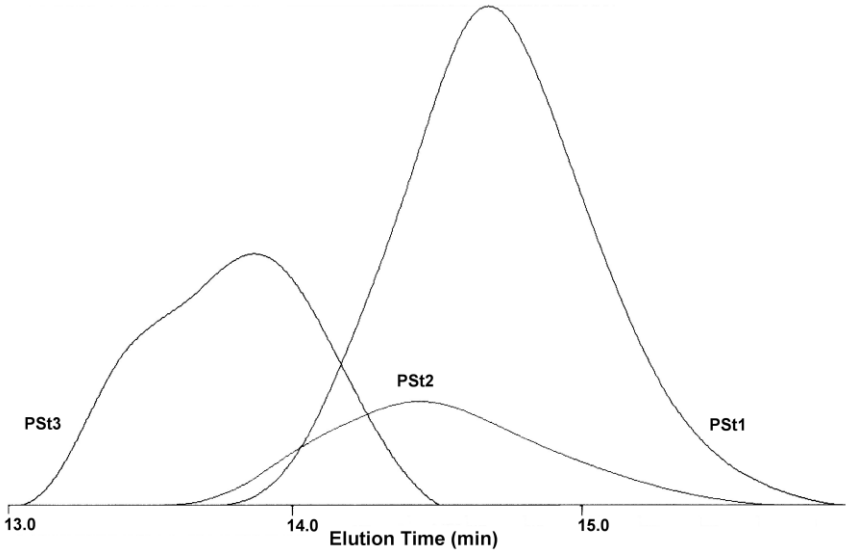


Figure 4.16 GPC traces of PSt1, PSt2, and PSt3.

The thermal properties of all the PSt's were evaluated by differencial scanning calorimetry (DSC) and thermogravimetry (TGA). The thermal behavior data of all PSt's are listed in Table 4.2. DSC measurements were conducted with a heating rate of 10 ^{0}C/min under nitrogen. The Tg values of the PSt's were in the range of 84-93 ^{0}C depending on the molecular weight increase. The Tg's of PSt can be seen in Figure 4.17.

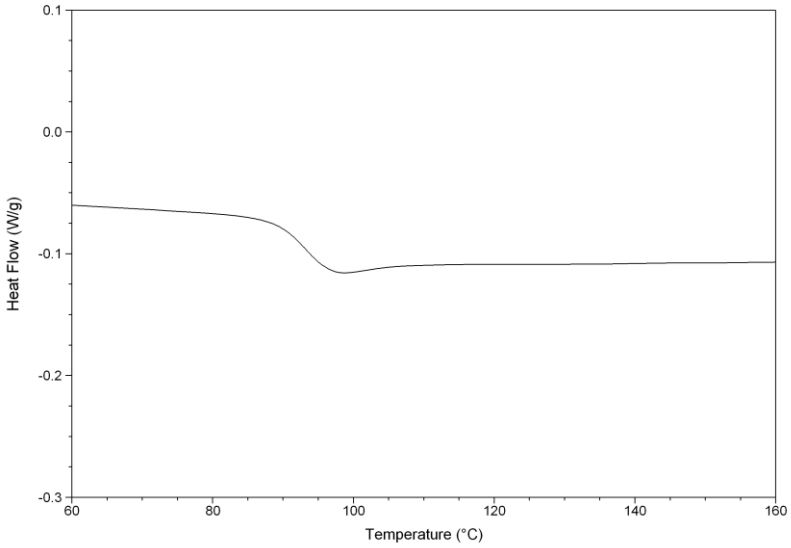


Figure. 4.17 DSC thermogram of PSt3

Table 4.2 Thermal properties of PSt.

Product	**[a]T_g ^{0}C**	**[b]TGA (%)**
PSt1	84,8	93,4
PSt2	89,4	93,3
PSt3	94,5	93,5
[c]STD PSt	100	97,2

[a]From the second heating traces of DSC measurements conducted with a heating rate of 10 ^{0}C/min under nitrogen.

[b]Weight loss was recorded by TGA at heating rate of 20 ^{0}C/min under nitrogen atmosphere at 500 ^{0}C.

[c]Polystyrene standard, Mn=19.000 g/mol.

The thermogravimetric behavior of the PSt was investigated in nitrogen. From TGA analysis all three of these polymers appear to possess enough thermal stability approximately 290 ^{0}C. Figure 4.18 shows the thermal stability and the weight change. Table 4.2 shows the weight changes of the PSt's at 500 ^{0}C.

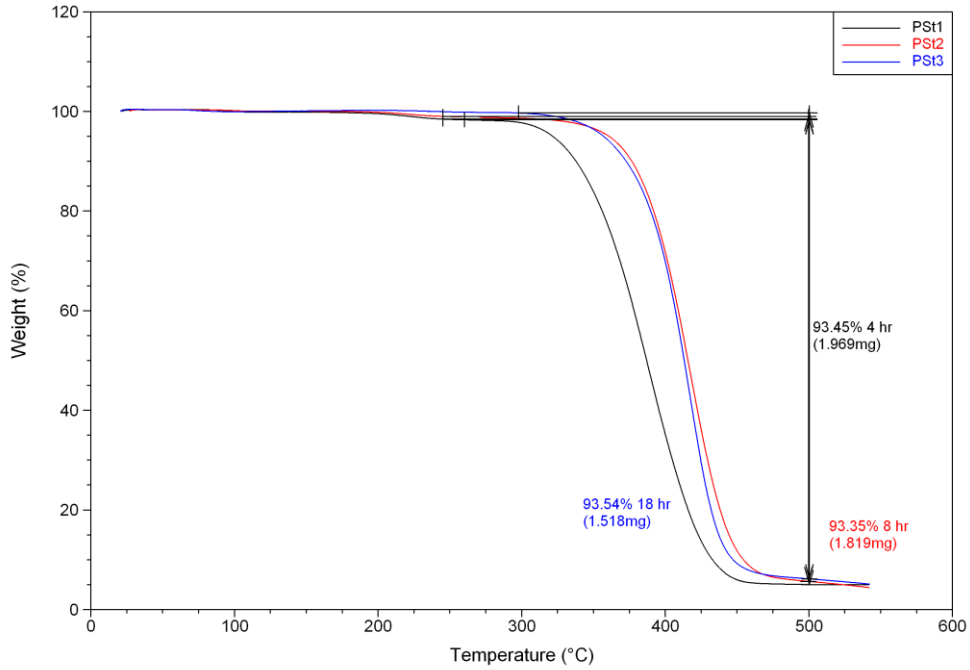


Figure 4.18 Thermogravimetric analysis of PSt under nitrogen.

To make a comparison we measured the T_g and TGA of standard PSt (Mn=19.000 g/mol). The T_g of the standard PSt is 100 ^{0}C and the weight loss is % 97. So the results shows us that the phosphorus containing PSt's char yield is higher than the standard PSt. The results can be seen in Table 4.2.

4.6 Preparation of Polymethyl methacrylate (PMMA) by ATRP mechanism using BBEPPO

Polystyrene homopolymer was polymerized via ATRP method depicted in Figure 4.19. Termination occured predominanatly by disproportionation then macroinitiators would have two functional bromine end groups. When a polymer chain contains an end group with an activated halogen atom, it can be used as a macroinitiator [39].

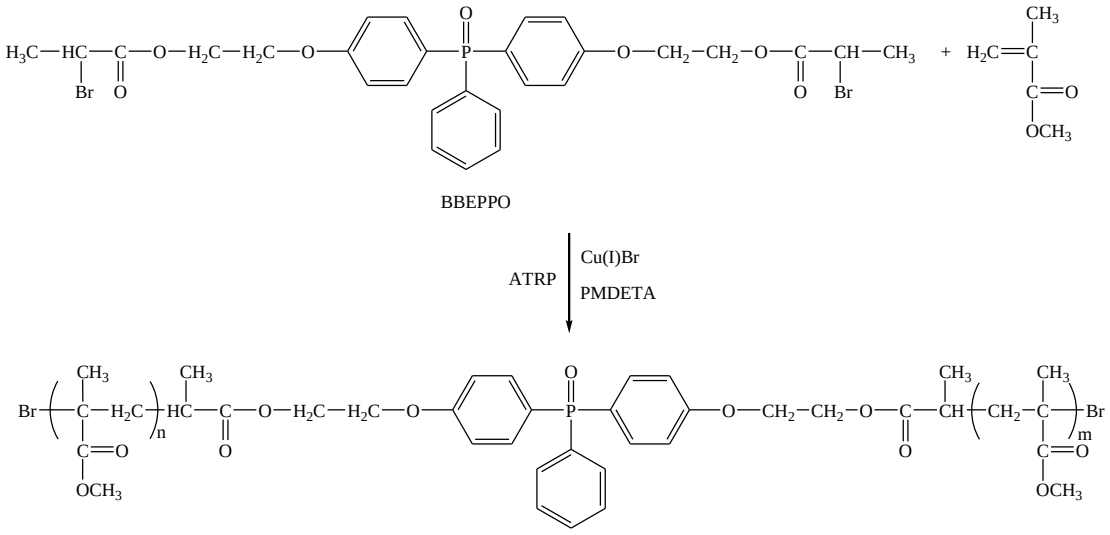


Figure 4.19 Synthesis scheme of PMMA

^{1}H-NMR Spectrum of PMMA as shown in Figure 4.20 was taken in $CDCl_3$. CH_3 protons at δ = 0,8-1,4 ppm, OCH_3 protons at δ = 3,5-3,9 ppm, and CH_2 protons at δ = 1,8-2,1 ppm.

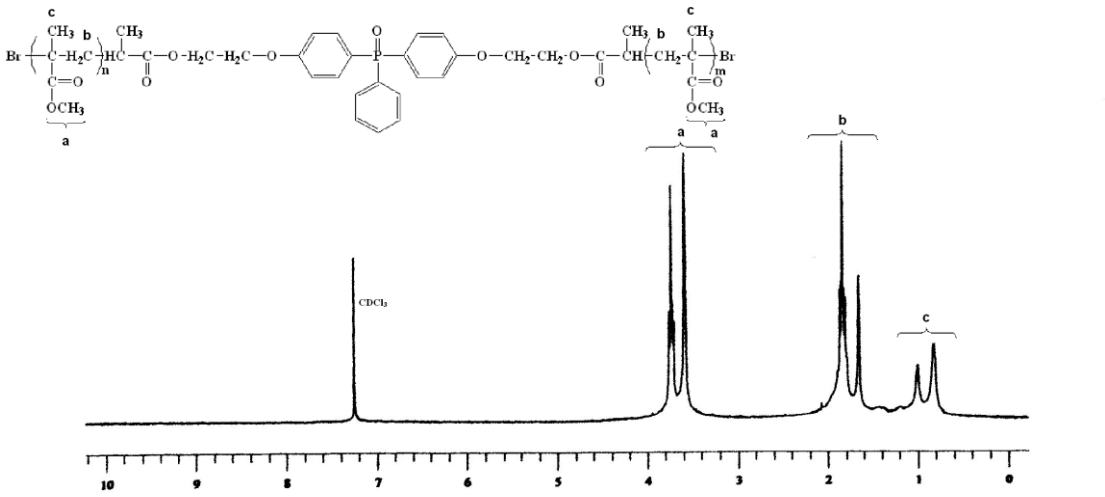


Figure 4.20 ^{1}H-NMR Spectrum of PMMA

Table 4.3 shows the percentage yield, molecular weight, and polydispersity index of the polymerized MMA as a function of reaction time in the presence of BBEPPO.

Table 4.3 ATRP of MMA by using BBEPPO[a]

Run No	[BEHPPO[a] (mol/L)	[M_o] (mol/l)	$[I_o]^b/[Cu^+]/[PMDETA]/[M_o^c$	Time (h)	Conv. (%)	M_n[d]	$M_{n(theo)}$[e]	M_w/M_n
PMMA1	0,06	6	1/1/2/100	4	45	12000	4500	1,65
PMMA2	0,06	6	1/1/2/100	8	57	16000	5700	1,46
PMMA3	0,06	6	1/1/2/100	18	90	24000	9000	1,3

[a]Temperature: 50 ^{0}C

[b]Initial initiator concentration

[c]Initial monomer concentration

[d]Determined by GPC based on PSt standarts

[e]Calculated by $[M_o]/[I_o] \times conv. \times M_{w\,(monomer)}$

Solvent : DMSO

At a reaction temperature of 50 ^{0}C, high amount of product yield was obtained. Molecular weight (M_n) aslo increased from 12000 to 24000 g/mol as the time increased from 4 to 18 h. The theoritical molecular weights ($M_{n(theo)}$) were calculated according to following equation.

$$[M_o]/[I_o] \times conv. \times M_{w\,(monomer)}$$

where $[M_o]$ and $[I_o]$ are the initial molar concentrations of the monomer and initiator, respectively and M_w is the molecular weight of the monomer [48].

The theoritical molecular weights of the resulting polymers was higher than the GPC values. This could be explained by the differences between polystyrene standarts.

The narrow molecular weight distributions were also obtained for PMMA1, PMMA2, and PMMA3 as shown in Figure 4.21.

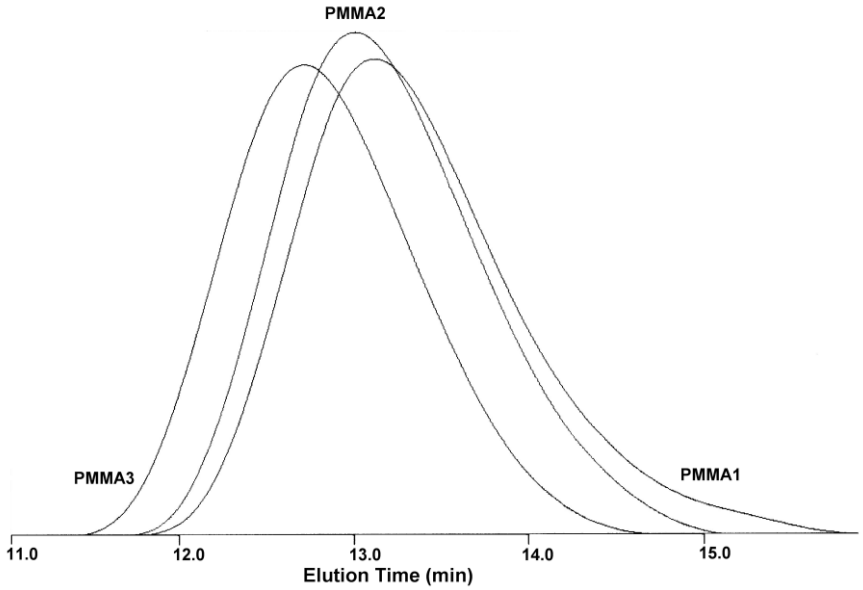


Figure 4.21 GPC traces of PMMA1, PMMA2, and PMMA3.

The thermal behavior of PMMA was studied by differencial scanning calorimetry (DSC). The Tg's of PMMA can be seen in Figure 4.22. Also it can be seen that T_g is increasing when the molecular weigt and the reaction time decrease.

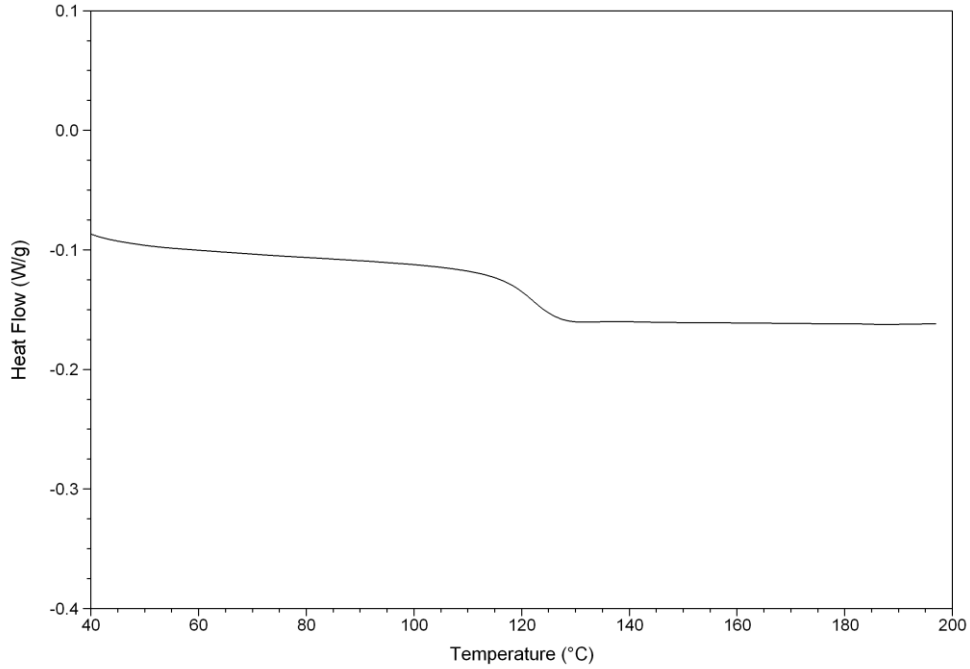


Figure. 4.22 DSC thermogram of PMMA3

Table 4.4 Thermal properties of PMMA.

Product	**[a]T_g ^{0}C**	**[b]TGA (%)**
PMMA1	112	97,3
PMMA2	120	96,2
PMMA3	122	97,5
[c]STD PMMA	122	97,2

[a]From the second heating traces of DSC measurements conducted with a heating rate of 10 ^{0}C/min under nitrogen.

[b]Weight loss was recorded by TGA at heating rate of 20 ^{0}C/min under nitrogen atmosphere at 500 ^{0}C.

[c]Polymethyl methacrylate standard, Mn=89.800 g/mol.

From TGA analysis all three of these polymers appear to possess enough thermal stability 190 ^{0}C. Figure 4.23 shows the thermal stability and the weight change. Table 4.4 shows the weight changes of the PMMA's at 500 ^{0}C.

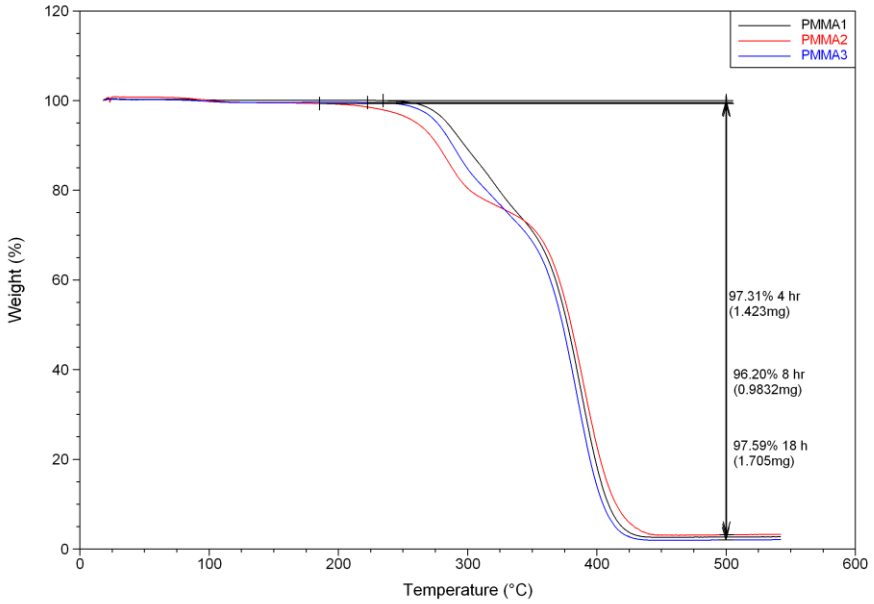


Figure.4.23 Thermogravimetric analysis of the PMMA under nitrogen.

As we have done in PSt, we measured the T_g and TGA of a standard PMMA (Mn=89.800 g/mol) to make a comparison with our results. The T_g of the Standard PMMA is 120 ^{0}C and the weight loss is %97. The results of the standard PMMA and the result of our PMMA's are similar. The results can be seen in Table 4.4.

5. CONCLUSIONS

A new original difunctional bromine functionalized triphenylphosphine oxide containing macroinitiator was synthesized.

This macroinitiator was used to initiate reactive bromine end functionalized PSt and PMMA via ATRP.

As a second step bromine end functionalized PSt and PMMA can be used to perform block copolymers via ATRP.

Synthesis of vinyl polymers with controlled molecular weight and narrow molecular weight distribution were obtained and characterized.

The T_g of the polymers increase accompanying the molecular weight increase.

The char yield of PSt is higher corresponding to PMMA and also the standard PSt.

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